Studies on New Radical Reactions of Organosilicon Compounds(Dissertation_全文)

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CHAPTER 1

Introduction and General Summary

Organosilicon compounds are widely used as materials and reagents because of their unique physical property and reactivity[1]. In modern organic synthesis, the development of highly selective and efficient reaction is one of the central problems. In order to achieve this object, a lot of organosilicon reagents and their reactions have been explored. The present thesis describes studies on several new radical reaction of organosilicon compounds with a view to throwing light on the effect of silyl group on radical reaction and developing highly selective and efficient organic synthetic methods.

Organosilanes have a long pedigree, although early investigations gave little clue to the potential now being realized. The first organosilane, tetraethylsilane, was prepared from tetrachlorosilane by Friedel and Crafts in 1863[2]. After that, Kipping performed the systematic studies on organosilane from 1898 to 1939[3]. The discovery and development of silicone polymers[4] led to the explosive growth of organosilicon chemistry over the past half century.

In organic synthesis, organosilicon reagents play a variety of roles, and the use for carbon-carbon bond formation is particularly important. For instance, allylsilanes[5] and silyl enolates[6] react with various electrophiles in the presence of Lewis acid to introduce allyl and carbonyl group. These reagents act as stable synthetic equivalents of the corresponding carbanion. In addition, the reaction of α-metallated organosilanes with carbonyl compounds is available for stereoselective synthesis of olefins as well as Wittig reaction[7]. More recently, the reaction of higher order silicate has been extensively studied aiming at more efficient carbon-carbon bond formation[8].

Since organotin reagents contain tin which belongs to the same group as silicon, the carbon-tin bond serves as a nucleophilic reaction center as well as carbon-silicon bond. In organotin chemistry, however, radical reactions mediated by tin radical are also important[9]. Use of organostannanes for generation of carbon radicals from a wide variety of functional groups has surfaced as a powerful strategy for synthesis. On the other hand, radical reactions with organosilicon reagents have been rarely used for organic synthesis, therefore, the effect of silyl group on carbon radical and the synthetic utilities of radical reactions of organosilion compounds are not well known.

It is well recognized that carbonium ions β and carbanions (or metalloid equivalents) α to silyl group are favored[10]. The β effect has been ascribed to (σ-p)π overlap between the bonding σ-level of the carbon-silicon bond with the adjacent empty p-orbital of the carbonium ion, whereas α-silyl carbanions are stabilized by (σ*-p)π overlap between the antibonding σ* level of the carbon-silicon bond with the adjacent filled p-orbital of carbanion, or highly polarized carbon-metal bond. Organosilicon chemistry based on these ionic effects has been extensively researched. Nucleophilic addition of allylsilanes and facile generation of α-metallated organosilanes are good examples utilizing these effects. In contrast, there had been little investigation of the stabilizing effect of silyl group on carbon radicals until recently[11]. The author gave attention to the rearrangement of cyclopropylmethyl radicals which produce more stable homoallyl radicals under predominant cleavage of one of two carbon-carbon bonds[12), 13)], and utilized this ring opening reaction for the examination of the stabilizing effect of silyl group on carbon radicals in Chapter 2.

Much attention has been paid to a method of introducing perfluoroalkyl groups to organic compounds from the view point of the development of new chemicals or materials[14], because they have distinguished characteristics such as

high electron-negativity, stability, and lipophilicity. The addition of perfluoroalkyl iodides to carbon-carbon multiple bonds is one of the most popular procedure to attach perfluoroalkyl chain to organic compounds. This reaction is catalyzed by transition metals, peroxides, or azobis(isobutyronitrile) (AIBN)[15], but these catalysts have some drawbacks in handling, efficiency, and reaction conditions. In the presence of a catalytic amount of oxygen molecule, however, the use of Et_3B solves these problems to promote perfluoroalkylation of olefins and acetylenes under mild condition[16]. Thus, the author examined Et_3B induced perfluoroalkylation of silyl enolates and ketene silyl acetals with perfluoroalkyl iodides to introduce perfluoroalkyl groups on α position of ketones and esters in Chapter 3[17]. The reaction of polyhalomethyl radical with ketene silyl acetals was also investigated in Chapter 4. Silyl enolates and ketene silyl acetals are easily synthesized from the corresponding ketones and esters[18]. These substrates are expected to be good acceptors of electrophilic polyhaloalkyl radicals because they are electron-rich olefins.

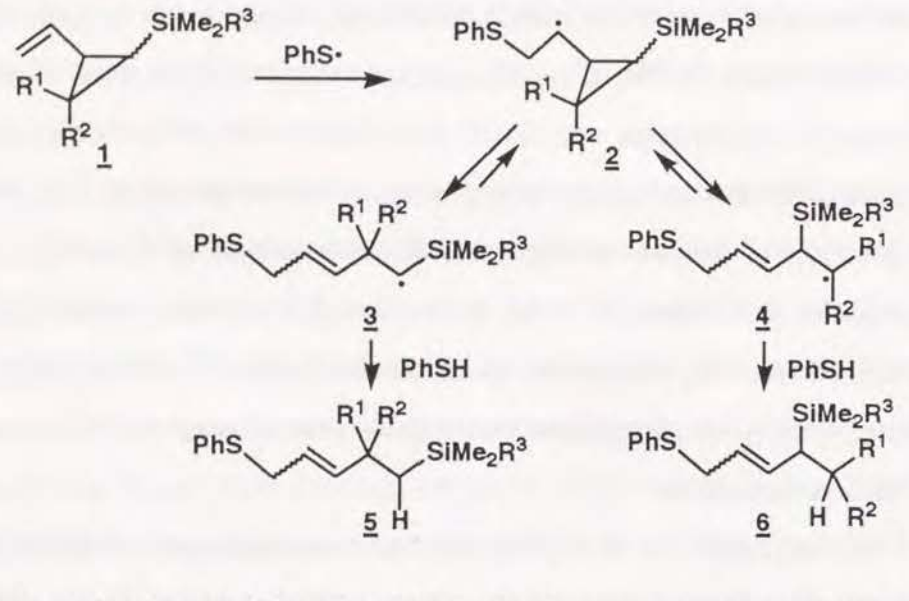
The synthetic use of silyl radical had been restricted to hydrosilylation of olefins and acetylenes catalyzed by various radical initiators[19]. In addition, the hydrosilylation has several difficult problems such as low yield, low stereoselectivity, and severe condition. Recently, tris(trimethylsilyl)silane (TTMSS) as an alternative to tri-*n*-butylstannane has become more popular[20], being a superior reagent from both ecological and practical perspectives. This silane can be used as a reducing agent for organic compounds or a hydrosilylating agent for multiple bonds in the presence of radical initiator. Then, the author investigated the radical reaction of acetylenes, dienes, and enynes with TTMSS in Chapter 5 and 6.

A brief general summary of the entire topics is as follows.

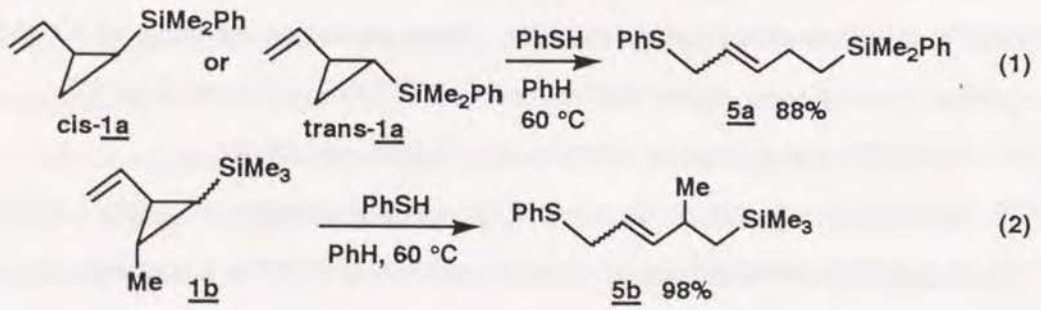
In Chapter 2, radical induced ring opening reaction of 1-trialkylsilyl-2-vinylcyclopropane **1** is described. Radical addition of PhSH to **1** is expected to form

homoallylsilane **5** and allylsilane **6** *via* cyclopropylmethyl radical **2** and homoallyl radical **3**, **4** (Scheme 1). It is predictable that the ratio of the two products **5**, **6** will reflect the stabilizing effect of the silyl group on the intermediary carbon radicals α to silicon (**3**) and β to silicon (**4**).

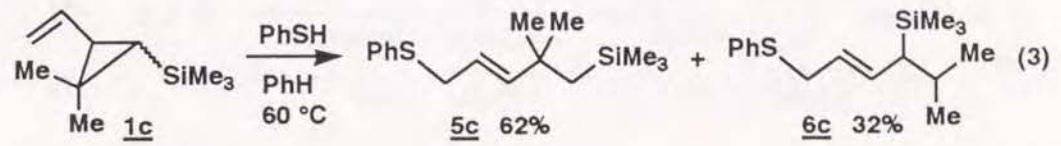
Scheme 1.



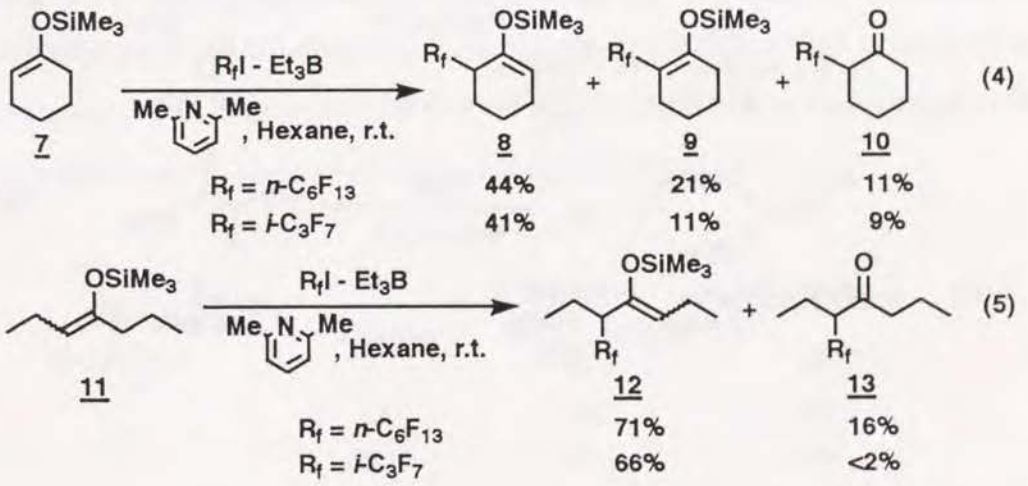
Reaction of 1-dimethylphenylsilyl-2-vinylcyclopropane (**1a**) with PhSH gave homoallylsilane **5a** and no trace of allylsilane **6a** was obtained in the reaction mixture (eq 1). The *cis*, *trans* stereochemistry of the cyclopropane did not affect the selectivity of the carbon-carbon bond fission. The use of methyl-substituted cyclopropane **1b** also afforded homoallylsilane **5b** selectively (eq 2).



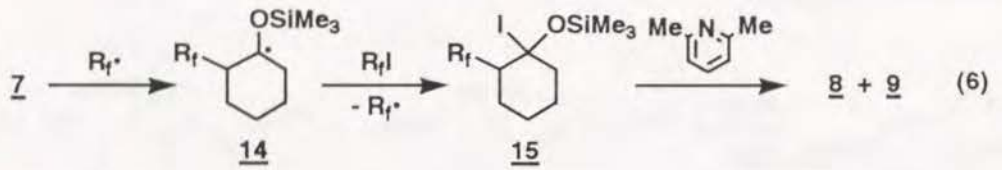
In contrast, the treatment of dimethyl-substituted cyclopropane with PhSH provided a mixture of homoallylsilane **5c** and allylsilane **6c** (**5c**/**6c** = 1.9/1, eq 3). These results support that silyl group stabilizes α-carbon radical more effectively than β-carbon radical, and carbon radical α to silyl group is slightly more stable than *t*-alkyl radical. Moreover, the reaction of cyclopropane bearing phenyl or acetyl group reveals that the stabilizing effect of the substituent is superior to that of trimethylsilyl group.



Chapter 3 discloses Et_3B induced perfluoroalkylation of silyl enolates and ketene silyl acetals with perfluoroalkyl iodides (R_fI). Reaction of silyl enolate **7** with *n*-$C_6F_{13}I$ or *i*-C_3F_7I in the presence of 2,6-dimethylpyridine and Et_3B gave perfluoroalkylated silyl enolates **8**, **9** and ketone **10** (eq 4). On the other hand, acyclic silyl enolate **11** provided only perfluoroalkylated silyl enolate **12** accompanied with ketone **13** (eq 5). Treatment of the reaction mixture with aqueous HCl afforded only **10** or **13** in good yield.

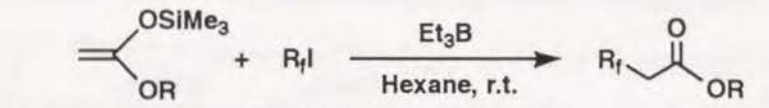


The following reaction mechanism is assumed to form perfluoroalkylated silyl enolates (eq 6). Perfluoroalkyl radical, generated by the action of ethyl radical on perfluoroalkyl iodide, adds to silyl enolate to give a radical **14**. The radical **14** abstracts iodine from R_fI to give an adduct **15** and regenerates perfluoroalkyl radical. The coexisting base causes the elimination of HI to give a mixture of perfluoroalkylated silyl enolates.

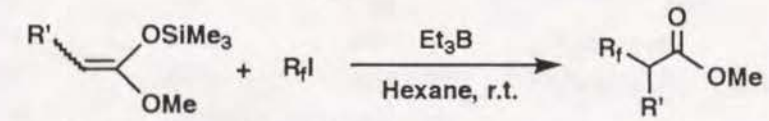


(6)

In the case of ketene silyl acetals, perfluoroalkylation proceeded easily without 2,6-dimethylpyridine. Ketene silyl acetal **16** derived from acetate reacted with various R_fI such as *n*-$C_6F_{13}I$, *i*-C_3F_7I and CF_3I to provide α-perfluoroalkylated ester **17** in high yields (eq 7). The reactivity of alkyl-substituted ketene silyl acetal **18** is lower than **16**, but the acetal **18** gave α-perfluoroalkylated ester **19** (eq 8).

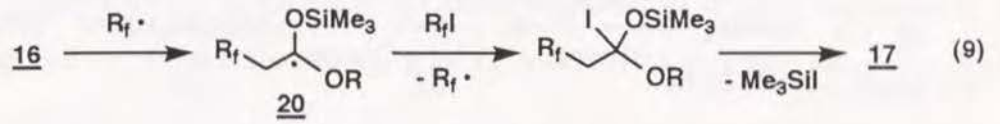


(7)

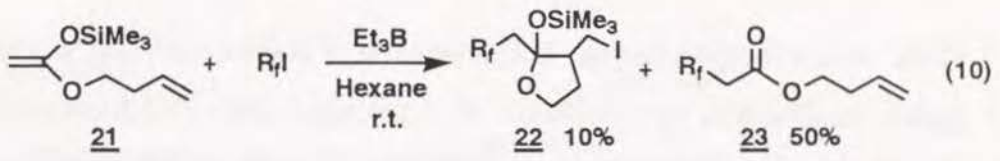


(8)

Plausible mechanism for the formation of α-perfluoroalkylated esters is shown in eq 9. To confirm this mechanism, ketene silyl acetal **21** was prepared from the corresponding ester. Reaction of the acetal with *n*-$C_6F_{13}I$ afforded a cyclized product **22** along with perfluoroalkylated ester **23** (eq 10). The formation of **22** suggests an intermediacy of carbon radical bearing alkoxy and siloxy groups **20**. The result also shows that carbon-carbon double bond of ketene silyl acetal is much more reactive than that of simple olefin.

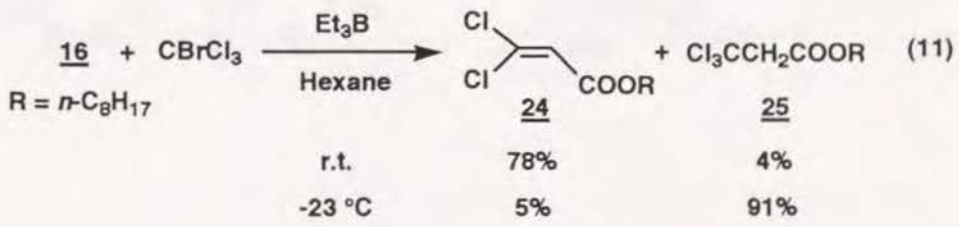


(9)



(10)

To explore applicability of the radical addition to ketene silyl acetals, several kinds of polyhalomethane are examined instead of R_fI in Chapter 4. Reaction of ketene silyl acetal **16** with $CBrCl_3$ produced 3,3-dichloroacrylates **24** at room temperature. In contrast, when the reaction was performed at -23 °C, 3,3,3-trichloropropanoates **25** were major products (eq 11). The use of alkyl-substituted ketene silyl acetal **18** afforded only 2-(trichloromethyl)octanoate **26** even at room temperature (eq 12). Not only $CBrCl_3$ but also CCl_4, CBr_4, and CF_2Br_2 can be used in these reactions to give the corresponding products.



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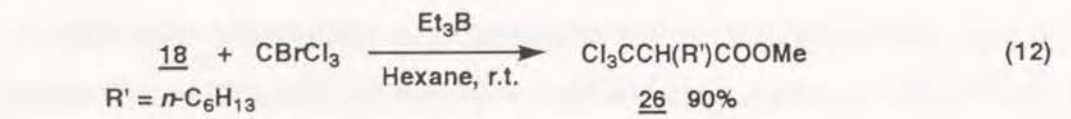
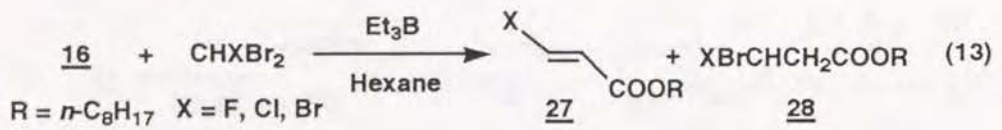


(12)

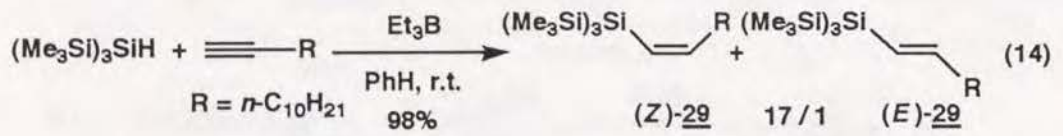
Meantime, trihalomethane such as $CHFBr_2$, $CHClBr_2$, and $CHBr_3$ reacted with ketene silyl acetal **18** in a similar fashion to give a mixture of (*E*)-3-haloacrylate **27** and 3,3-dihalopropanoate **28** (eq 13). By treatment of the mixture with Et_3N, **27** was obtained exclusively in good yields.



(13)

These results indicate that the radical addition of polyhalomethane to ketene silyl acetal is effective for synthesis of 3,3-dihalo- and (*E*)-3-haloacrylates.

Chapter 5 is concerned with stereoselective radical addition of trialkylsilane to acetylenes and stereoselective reduction of alkenyl iodides with tris(trimethylsilyl)-silane. Et_3B induced hydrosilylation of 1-dodecyne was examined using various silanes such as Ph_3SiH, Ph_2SiH_2, $Me_3SiSiPh_2H$, $(Me_3Si)_2SiPhH$, and $(Me_3Si)_3SiH$ (TTMSS). Reaction of each hydrosilane with 1-dodecyne at room temperature provided the corresponding alkenylsilane. TTMSS proved to be the best reagent for hydrosilylation and afforded (*Z*)-1-[tris(trimethylsily)silyl]-1-dodecene **29** in excellent yield and selectivity ((*Z*)/(*E*) = 17/1, eq 14).



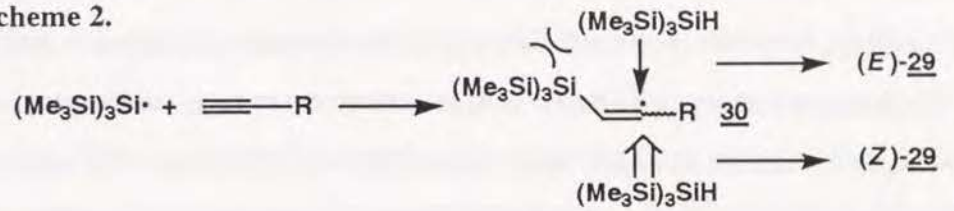
(14)

The stereoselectivity of product depends on the reaction conditions. Whereas treatment of a benzene solution of 1-dodecyne with TTMSS in the presence of AIBN at reflux gave a mixture of (*Z*)- and (*E*)-**29** ((*Z*)/(*E*) = 4/1), Et_3B initiated reaction at 0 °C provided (*Z*)-**29** almost exclusively ((*Z*)/(*E*) > 20/1).

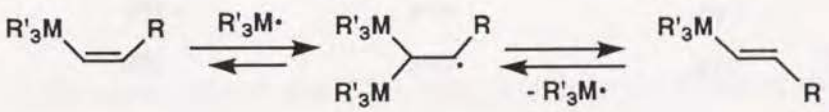
Next, the reaction of various alkynes with TTMSS has been examined. Although monosubstituted acetylenes produced the corresponding alkenylsilane in good to excellent yield with high (*Z*)-stereoselectivity, internal acetylene such as 6-dodecyne did not undergo hydrosilylation.

The selective formation of (*Z*)-alkenylsilane is due to steric hindrance of silyl group which prevents the *syn* attack of silane in the intermediary alkenyl radical **30** (Scheme 2).

Scheme 2.

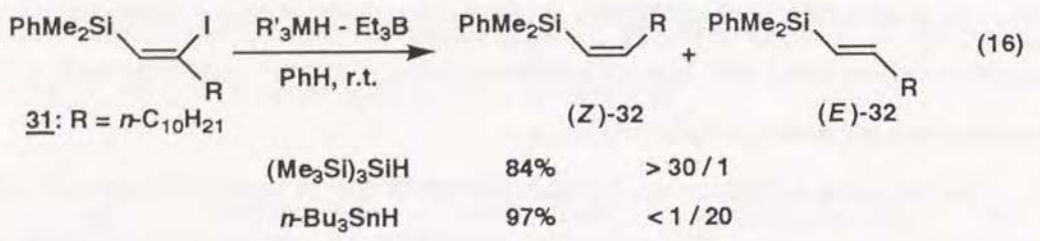


Unlike hydrosilylation, hydrostannylation and hydrogermylation catalyzed by Et_3B give (*E*)-alkene at room temperature because the addition-elimination of germyl or stannyl radical causes isomerization of (*Z*)-product into (*E*)-isomer (eq 15). In hydrosilylation with TTMSS, the isomerization of (*Z*)-alkenylsilane by tris(trimethylsilyl)silyl radical do not proceed. Then, the author applied the TTMSS-Et_3B system to stereoselective reduction of alkenyl iodides.

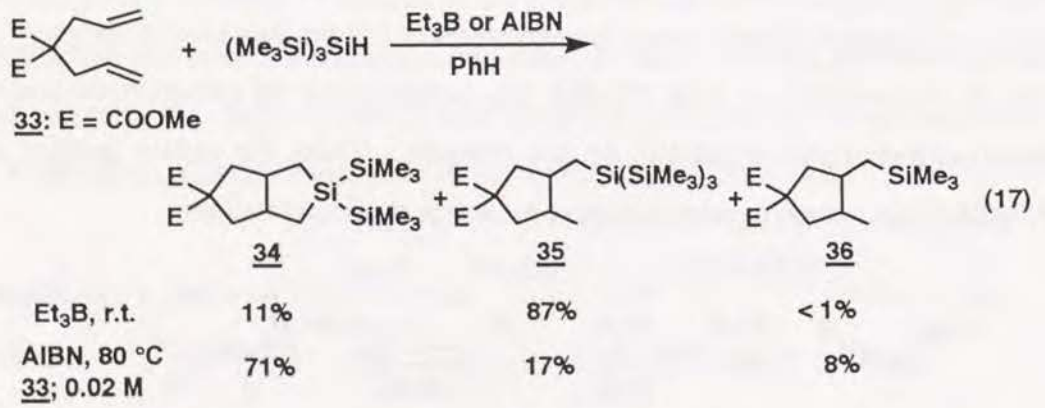


(15)

Reduction of alkenyl iodide **31** with TTMSS-Et_3B gave (*Z*)-alkenylsilane **32** predominantly. In contrast, by the use of *n*-Bu_3SnH instead of TTMSS, (*E*)-**32** was obtained as a major product (eq16). Thus, the stereoselectivity of product can be controlled by the change of reducing agent.

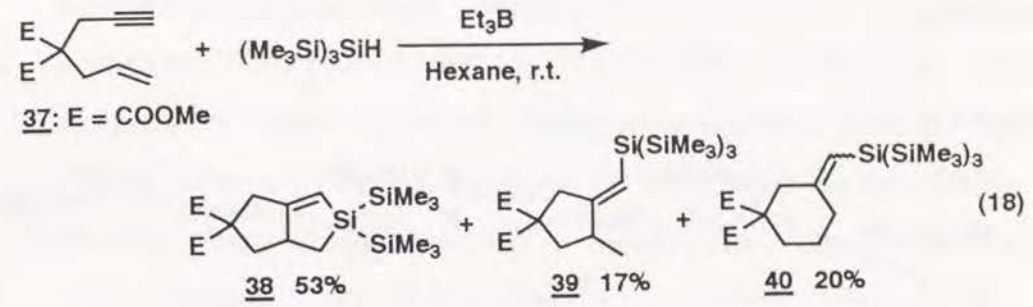


Chapter 6 deals with tris(trimethylsilyl)silyl radical induced bicyclization of 1,6-dienes and 1,6-enynes. 1,6-Diene **33** reacted with TTMSS in the presence of Et_3B to afford bicyclo compound **34** along with expected cyclopentane derivative **35**. The reaction was repeated under various conditions to increase the yield of **34**. In consequence, the use of AIBN under high dilution condition gave **34** selectively. Under this reaction condition, trimethylsilylmethyl-substituted cyclopentane **36** was also obtained in addition to the formation of **34** and **35** (eq 17).



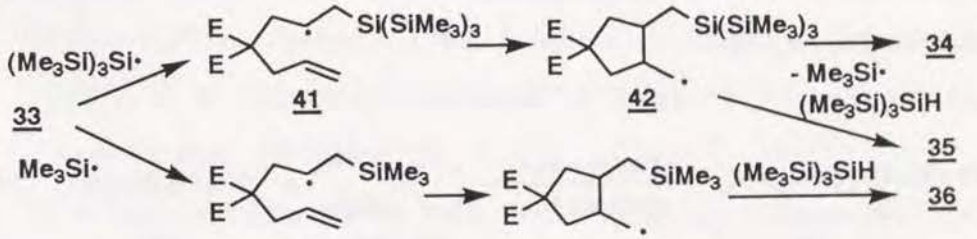
Treatment of 1,6-enyne **37** with TTMSS-Et_3B provided bicyclo compound **38**

as a major product along with methylenecyclopentane **39** and methylenecyclohexane **40** (eq 18). The change of reaction condition failed to improve the yield of **38**.



The reasonable mechanism for bicyclization of dienes and enynes is described in Scheme 3 and 4. Tris(trimethylsilyl)silyl radical attacks terminal olefinic carbon of 1,6-diene **33** to give a carbon radical **41**, which cyclized to cyclopentylmethyl radical **42**. The carbon radical attacks silicon having three trimethylsilyl groups to produce **34** under generation of trimethylsilyl radical. The formation of **36** supports the intermediacy of trimethylsilyl radical.

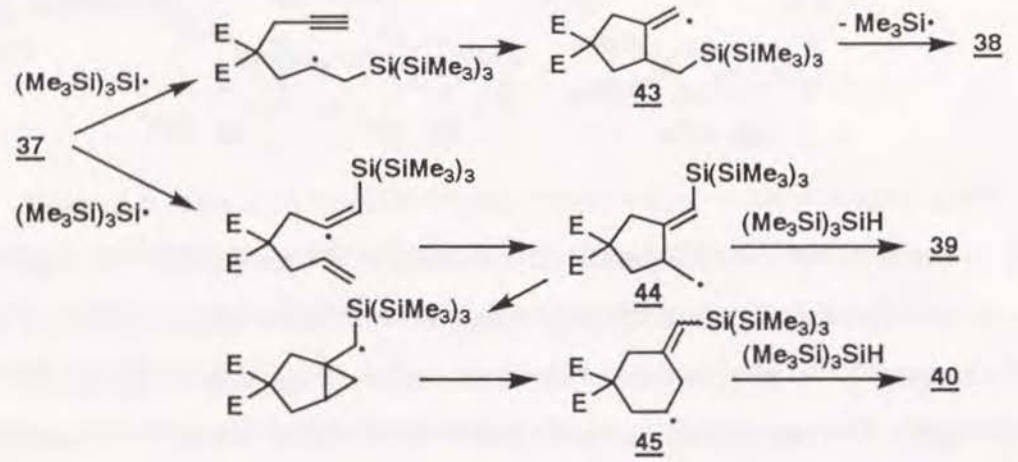
Scheme 3.



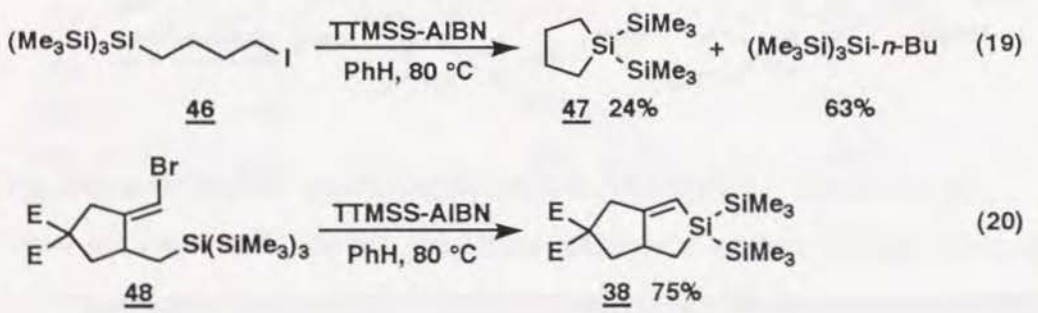
In the case of 1,6-enyne **37**, tris(trimethylsilyl)silyl radical can attack either terminal olefinic carbon or terminal acetylenic carbon. The attack on terminal olefinic carbon gives **38** *via* olefinic radical **43**. On the other hand, an addition of

tris(trimethylsilyl)silyl radical to terminal acetylenic carbon provides cyclopentylmethyl radical **44** which can not undergo cyclization because of its (*E*)-stereochemistry. Thus, the radical **44** abstracts hydrogen from TTMSS to provide **39**. Alternatively, **44** rearranges to cyclohexyl radical **45** which reacts with TTMSS to give **40.**

Scheme 4.



To confirm the silicon-silicon bond fission by homolytic substitution, iodoalkylsilane **46** and vinylbromide **48** were prepared. Reaction of **46** or **48** with TTMSS-AIBN afforded silacyclopentane **47** or silabicyclo compound **38** respectively (eq 19, 20).



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Instrumentation and Materials

Distillation of the products was performed by use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. Melting point was obtained on a Yanako MP-50929 melting point apparatus and are uncorrected, too. ^{1}H NMR and ^{13}C NMR spectra were taken on a Varian XL 200 or a Varian GEMINI 300 spectrometer, and chemical shifts are expressed in ppm downfield from internal tetramethylsilane using the δ scale. ^{19}F NMR spectra were recorded on JEOL JNM-FX 90Q spectrometer and the chemical shifts are given in δ with $CFCl_3$ as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer and the mass spectra on a Hitachi M-80 machine. Column chromatography was done with silica-gel (Wakogel 200 mesh). Analytical and preparative GLPC were performed with a Shimadzu Gas Chromatograph, Model GC-8A using thermal conductivity detector and helium as carrier gas. Liquid chromatography (LC) was performed with Japan Analytical Industry Co., Ltd. LC-908 using $CHCl_3$ as an eluent. Elemental analyses were performed by the staff at the Elemental Analyses Center of Kyoto University.

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Benzene, hexane and diethyl ether were dried over a slice of sodium. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use.

Abbreviations

Ac	acetyl	mmol	millimole
AIBN	azobis(isobutyronitrile)	mp	melting point
bp	boiling point	MS	mass (spectrum)
bs	broad singlet	NMR	nuclear magnetic resonance
Bu	butyl	p. (pp.)	page(s)
ca.	circa (about)	PCC	pyridinium chlorochromate
calcd	calculated	Ph	phenyl
Co.	company	PLC	preparative TLC
concd	concentrated	Pr	propyl
d	doublet	q	quartet
dec	decomposed	ref	reference
DMSO	dimethyl sulfoxide	R_f	perfluoroalkyl
Ed.	edition	R_f	relative mobility
eq	equation	r.t.	room temperature (25 ± 3 °C)
equiv	equivalent	s	singlet
Et	ethyl	sep	septet
GLPC	gas liquid phase chromatography	t	triplet
		temp	temperature
h	hour(s)	THF	tetrahydrofuran
ibid.	*ibidem* (in the same space)	THP	tetrahydropyranyl
IR	infrared (spectrum)	TLC	thin layer chromatography
LC	liquid chromatography	TMS	trimethylsilyl
m	multiplet	Torr	1 Torr = 133.322 Pa
M	molar (1 M = 1 mol dm^{-1})	t_r	retention time
Me	methyl	Ts	toluenesulfonyl
min	minute(s)	TTMSS	tris(trimethylsilyl)silane
mL	1 mL = 1 cm^{-3}		

CHAPTER 2

Synthesis and Radical Induced Ring Opening Reaction of 1-Trialkylsilyl-2-vinylcyclopropanes

A variety of trialkylsilylvinylcyclopropanes were prepared by two different routes: (a) Cyclopropanation of 1-alkenylsilanes and (b) the reactions of 1-bromocyclopropyllithium with trimethylsilyl chloride. Radical induced ring opening reaction of these cyclopropanes were examined. 1-Dimethylphenylsilyl-2-vinylcyclopropane or 3-methyl-1-trialkylsilyl-2-vinylcyclopropane provided the corresponding homoallylic silane exclusively upon treatment with PhSH, Ph_3SnH, n-Bu_3SnH, or n-$C_6F_{13}I$. On the other hand, 2-phenyl-1-trimethylsilyl-3-vinyl-cyclopropane or 2-acetyl-1-trimethylsilyl-3-vinylcyclopropane gave allylic silane selectively.

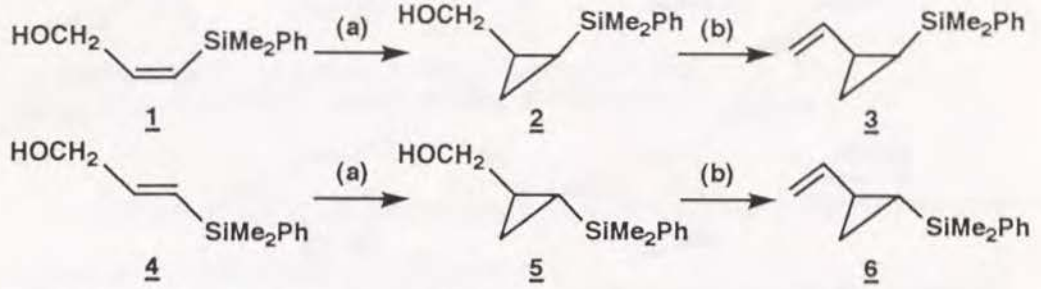
Trimethylsilyl substituent behaves in a dichotomous manner, showing the properties of both electron donor and acceptor groups. α-Trimethylsilyl carbanions are stabilized by (σ^*-p)π overlap between the antibonding σ^* level of the C-Si bond with the adjacent filled p-orbital of the carbanion, or highly polarized carbon-metal bond, whereas reactions which involve carbonium ion formation or development β to silicon are positively encouraged. Organosilicon chemistry based on these ionic effects has been extensively studied.[1] In contrast, there has been little investigation of the stabilizing effect of trimethylsilyl group on carbon radicals.[2] By using 3-substituted 1-trimethylsilyl-2-vinylcyclopropanes as models of free radical substituent effects we found that α-trimethylsilyl stabilization was substantial.[3]

(1) Synthesis of 1-Trialkylsilyl-2-vinylcyclopropanes. In recent years, increasing interest has been devoted to the chemistry of silicon containing molecules and much effort has been made to introduce the silyl moiety into organic compounds. Several methods are known for the synthesis of trimethylsilylcyclopropanes.[4-8] Here we want to describe two different routes to the title 1-trialkylsilyl-2-vinylcyclopropanes: (a) Cyclopropanation of 1-alkenylsilanes and (b) the reaction of 1-bromocyclopropyllithium with trimethylsilyl chloride.

Treatment of (*Z*)-3-dimethylphenylsilyl-2-propen-1-ol (**1**) with CH_2I_2-Et_2Zn[9] in diisopropyl ether gave *cis*-cyclopropane **2** in 60% yield. Swern oxidation[10] followed by Wittig methylenation afforded *cis*-1-dimethylphenylsilyl-2-vinylcyclopropane (**3**). *Trans*-isomer **6** was prepared starting from (*E*)-3-dimethylphenylsilyl-2-propen-1-ol (**4**) following the same procedure (Scheme 1).

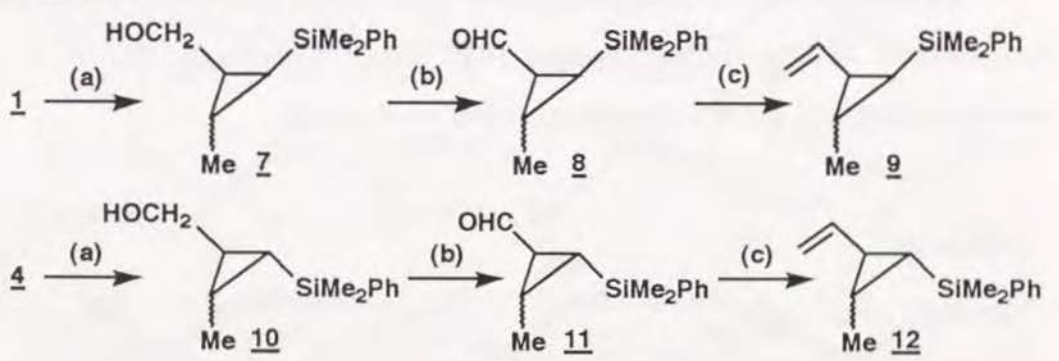
Synthesis of methyl-substituted cyclopropanes were performed by the reaction of olefins **1** and **4** with CH_3CHI_2-Et_2Zn.[11] The reaction yielded predominantly *trans*-isomer. Thus, (*Z*)-alcohol **1** gave a 25:1 mixture **7** of *r*-1-dimethylphenylsilyl-*c*-2-hydroxymethyl-*t*-3-methylcyclopropane and *r*-1-dimethylphenylsilyl-*c*-2-hydroxymethyl-*c*-3-methylcyclopropane. In the meantime, (*E*)-alcohol **4** gave a 7:4 mixture **10** of *r*-1-dimethylphenylsilyl-*t*-2-hydroxymethyl-*t*-3-methylcyclopropane and *c*-3-methylcyclopropane. Oxidation and successive methylenation afforded the corresponding vinylcyclopropanes **9** and **12** (Scheme 2).

Scheme 1.



(a) CH_2I_2 - Et_2Zn (b) 1) DMSO, $(COCl)_2$ 2) $Ph_3P{=}CH_2$

Scheme 2.

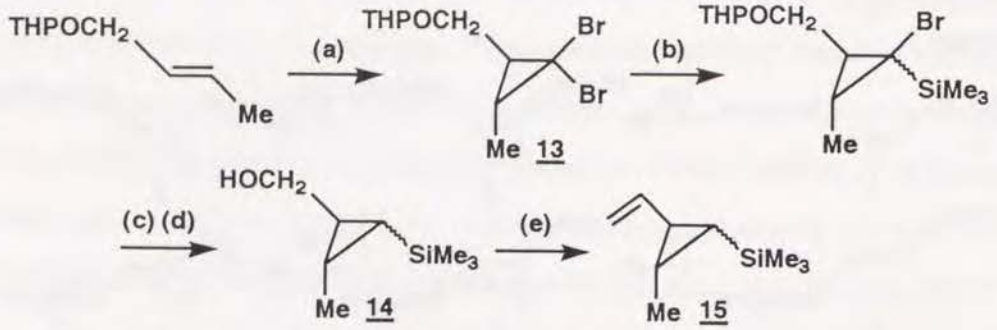


(a) CH_3CHI_2, Et_2Zn (b) DMSO, $(COCl)_2$ (c) $Ph_3P{=}CH_2$

Alternatively, trimethylsilylcyclopropanes were prepared from 1,1-dibromocyclopropanes. An Addition of butyllithium to a mixture of 1,1-dibromocyclopropane **13** and large excess of trimethylsilyl chloride at -107 °C in tetrahydrofuran provided 1-bromocyclopropyltrimethylsilane.[5] Treatment of crude product with *n*-Bu_3SnH-Et_3B[12] followed by deprotection of tetrahydropyranyl ether gave a

1.8:1 mixture of **14** in 71% yield from **13**. Oxidation followed by Wittig methylenation provided the desired 1-trimethylsilyl-2-vinyl-3-methylcyclopropane **15** (Scheme 3).

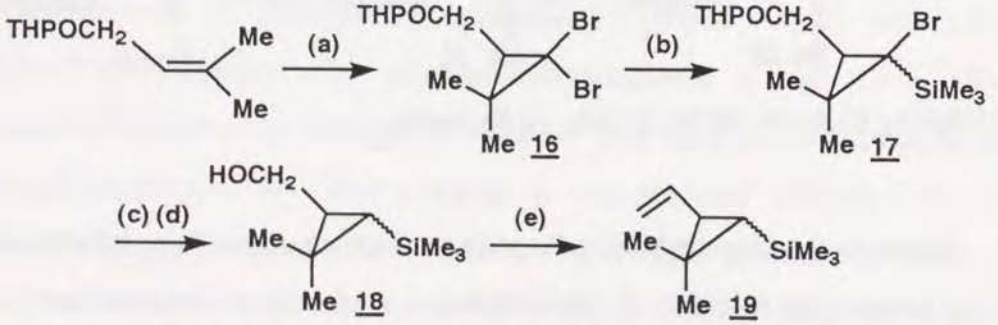
Scheme 3.



(a) $CHBr_3$, *t*-BuOK (b) *n*-BuLi, TMSCl (c) *n*-Bu_3SnH, Et_3B
(d) *p*-TsOH, MeOH (e) 1) DMSO, $(COCl)_2$ 2) $Ph_3P{=}CH_2$

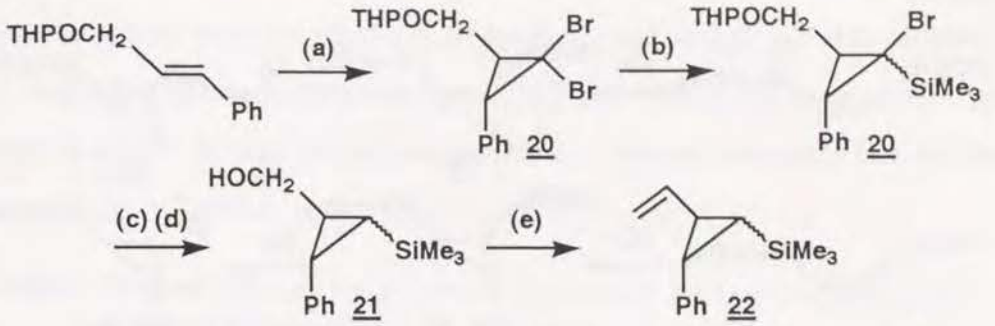
In similar fashion, dimethyl-substituted cyclopropane **19** or phenyl-substituted cyclopropane **22** was prepared starting from tetrahydropyranyl ether of prenyl alcohol or cinnamyl alcohol, respectively (Scheme 4 and 5).

Scheme 4.



(a) $CHBr_3$, *t*-BuOK (b) *n*-BuLi, TMSCl (c) *n*-BuLi, AcOH or *n*-Bu_3SnH, Et_3B
(d) *p*-TsOH, MeOH (e) 1) DMSO, $(COCl)_2$ 2) $Ph_3P{=}CH_2$

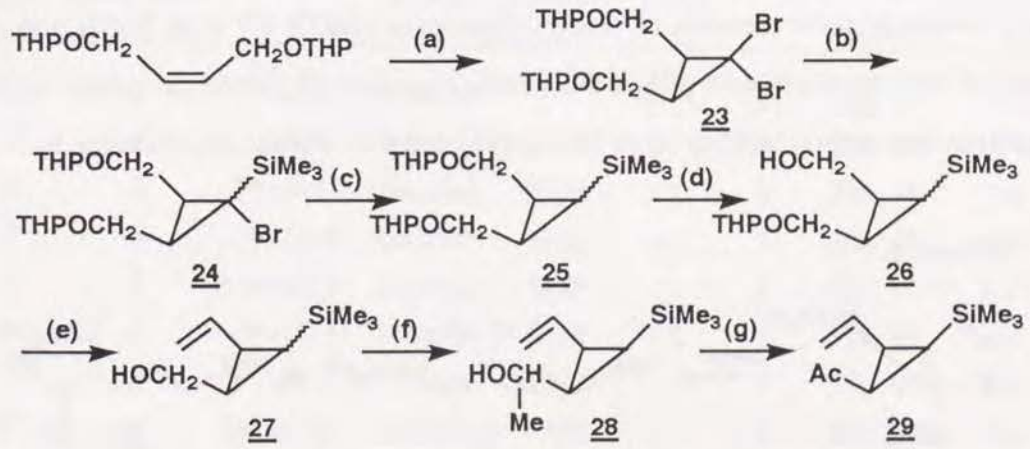
Scheme 5.



(a) $CHBr_3$, *t*-BuOK (b) *n*-BuLi, TMSCl (c) *n*-Bu_3SnH, Et_3B
(d) *p*-TsOH, MeOH (e) 1) DMSO, $(COCl)_2$ 2) $Ph_3P{=}CH_2$

Acetylcyclopropane **29** was prepared from bis(2-tetrahydropyranyl) ether of *cis*-2-butene-1,4-diol as shown in Scheme 6.

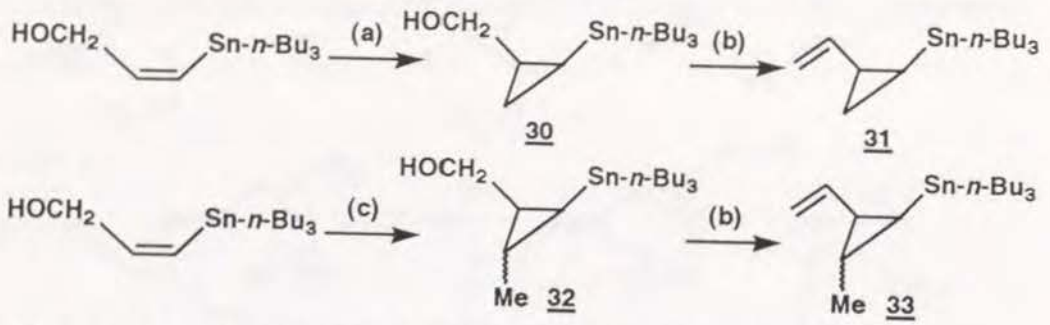
Scheme 6.



(a) $CHBr_3$, *t*-BuOK (b) *n*-BuLi, TMSCl (c) *n*-Bu_3SnH, Et_3B (d) *p*-TsOH, MeOH
(e) 1) DMSO, $(COCl)_2$ 2) $Ph_3P{=}CH_2$ 3) *p*-TsOH, MeOH (f) 1) DMSO, $(COCl)_2$
2) MeMgI (g) PCC

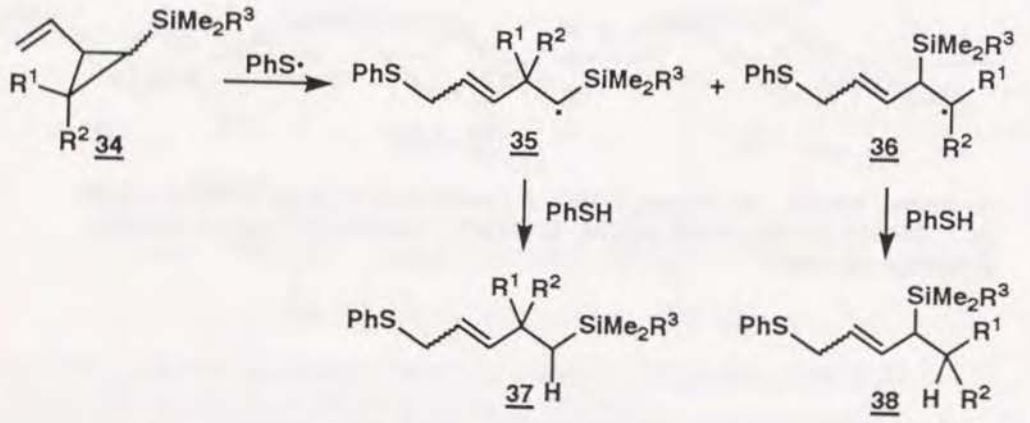
Tributylstannylvinylcyclopropanes were also prepared by the following sequences (Scheme 7).

Scheme 7.



(2) Radical Induced Ring Opening Reaction of 1-Trialkylsilyl-2-vinylcyclopropanes. A priori, it is predictable that two isomers, homoallylic silane (**37**, $PhSCH_2CH{=}CHCR^1(R^2)CH_2SiMe_2R^3$) and allylic silane (**38**, $PhSCH_2CH{=}CHCH(SiMe_2R^3)CHR^1R^2$) will be generated under cyclopropane ring cleavage in the reaction of vinylcyclopropane (**34**)[13, 14] with PhSH and the ratio of two products will reflect the stabilizing effect of R^3Me_2Si group on the intermediary carbon radicals (α to silicon (**35**) and β to silicon (**36**))(Scheme 8).

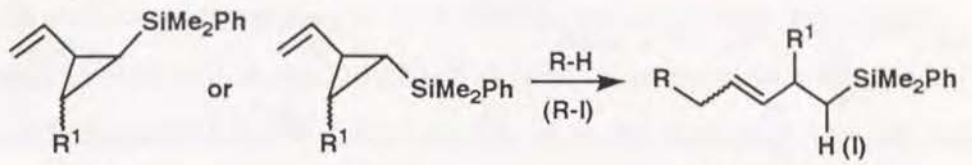
Scheme 8.



Treatment of *cis*-1-dimethylphenylsilyl-2-vinylcyclopropane (**3**) with PhSH

at 60 °C in benzene provided homoallylic silane (**39a**, *E*/*Z* = 9/1) in 88% yield. Other reagents such as Ph_3SnH, *n*-Bu_3SnH, and *n*-$C_6F_{13}I$ also afforded the corresponding homoallylic silanes in the Et_3B-induced radical reaction[12,15], and no trace of allylic silanes were observed in the reaction mixture. The results are summarized in Table 1.

Table 1. Radical-Induced Ring Opening Reaction of 1-Dimethylphenylsilyl-2-vinylcyclopropane[a)]

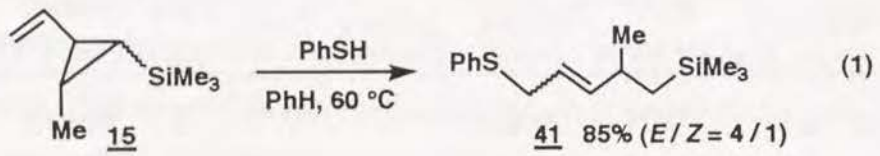


Entry	Substrate	R-H or R-I	Solvent	Initiator	Temp	Time / h	Product: Yield / %	*E*/*Z*[b)]
1	**3**	PhSH	benzene	—	60 °C	3	**39a**: 88	9/1
2	**6**	PhSH	benzene	—	60 °C	5	**39a**: 88	5/1
3	**3**	Ph_3SnH	benzene	Et_3B	r.t.	1	**39b**: 96	7/2
4	**6**	Ph_3SnH	benzene	Et_3B	r.t.	1	**39b**: 95	5/3
5	**3**	*n*-Bu_3SnH	benzene	Et_3B	r.t.	1	**39c**: 86	10/3
6	**6**	*n*-Bu_3SnH	benzene	Et_3B	r.t.	1	**39c**: 92	4/3
7	**3**	*n*-$C_6F_{13}I$	hexane	Et_3B	r.t.	3	**39d**: 91	50/1
8	**6**	*n*-$C_6F_{13}I$	hexane	Et_3B	r.t.	3	**39d**: 93	8/1
9	**9**	PhSH	benzene	—	60 °C	1	**40a**: 90	18/1
10	**12**	PhSH	benzene	—	60 °C	3	**40a**: 90	8/1
11	**9**	Ph_3SnH	benzene	Et_3B	r.t.	0.5	**40b**: 79	8/1
12	**12**	Ph_3SnH	benzene	Et_3B	r.t.	2	**40b**: 88	7/2

a) Silylcyclopropane (**3**, **6**, **9**, and **12**, 1.0 mmol) and R-H or R-I (1.1 mmol) were employed in the absence or presence of Et_3B (0.2 mmol). b) Determined by ^1H NMR.

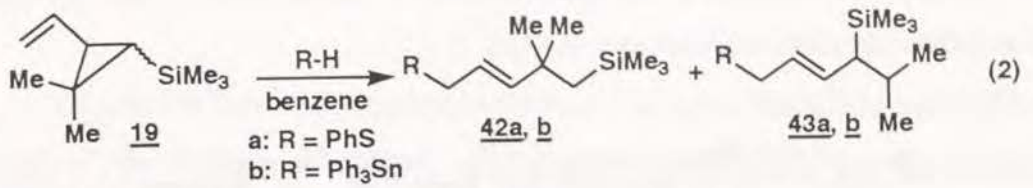
The *cis, trans* stereochemistry of the cyclopropane did not affect the selectivity of the C-C bond fission. *Cis*-isomer **3** as well as *trans*-isomer **6** provided the same homoallylic silane **39** as a single regioisomer, although the *E, Z* ratios of the products **39** derived from **3** were slightly different from those generated from **6**. For instance, *cis*-isomer **3** provided a mixture of (*E*)- and (*Z*)-5-dimethylphenylsilyl-1-phenylthio-2-pentene in a 9:1 ratio upon treatment with benzenethiol, whereas trans isomer **6** gave a mixture of *E*/*Z* = 5/1.

Methyl-substituted cyclopropane **9**, **12**, or **15** gave homoallylic silane **40** or **41** exclusively upon treatment with PhSH or Ph_3SnH (Table 1. Entries 9-12 and eq 1). Again, one of two carbon-carbon bonds was broken selectively independent of the stereochemistry of the substrate. Thus, both *cis*-isomer **9** and *trans*-isomer **12** afforded the same homoallylic silane **40.**



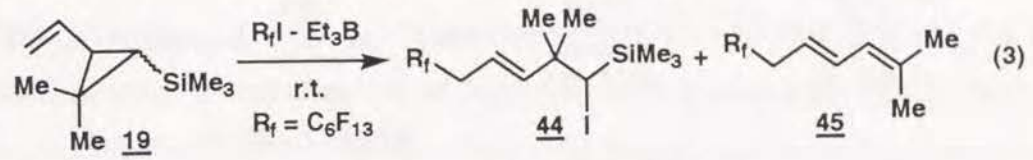
(1)

Exposure of dimethyl-substituted trimethylsilylcyclopropane **19** to PhSH provided a mixture of homoallylic silane **42a** and allylic silane **43**a (**42a**/**43a** = *ca.* 2/1) in 94% combined yield. In the case of *n*-$C_6F_{13}I$ as a reagent, 5-methyl-1-tridecafluorohexyl-2,4-hexadiene (**45**) was obtained instead of 5-iodo-5-methyl-1-tridecafluorohexyl-4-trimethylsilyl-2-hexene because (β-iodoalkyl)trimethylsilane was extremely unstable with respect to β elimination. The stereochemistry of the cyclopropane **19** did not affect the ratios of the product **42**/**43** (or **44**/**45**) so much. (*E*)-isomers were obtained exclusively in the reactions of **19** with PhSH, Ph_3SnH, and *n*-$C_6F_{13}I$ as shown in eq 2 and 3.



(2)

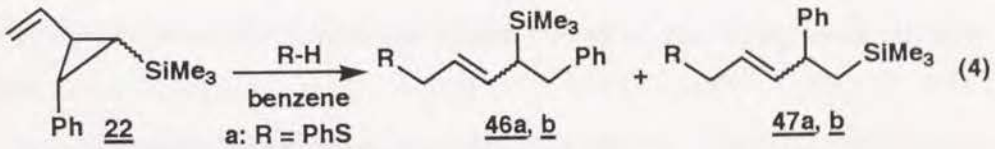
trans / cis of 19	Reaction Conditions	42 / 43
20 / 1	PhSH, 60 °C, 8 h	1.9 / 1
1 / 3.8	PhSH, 60 °C, 1 h	2.2 / 1
20 / 1	Ph_3SnH-Et_3B, r.t., 2 h	2.0 / 1



(3)

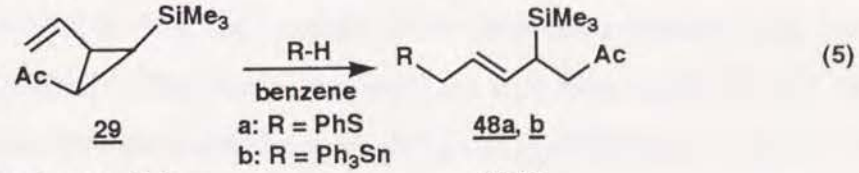
trans / cis of 19	Reaction time	Yield	44 / 45
20 / 1	7 h	62%	1.8 / 1
1 / 3.8	5 h	47%	2.6 / 1

Two other vinylcyclopropanes (**22** and **29**) were treated with PhSH or Ph_3SnH-Et_3B. The results showed that phenyl group or acetyl group stabilized the radical on adjacent carbon[16] more strongly than trimethylsilyl group (eq 4 and 5).



(4)

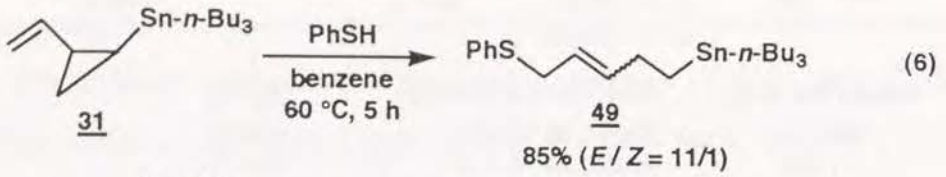
Reaction conditions	Yield	46 (*E* / *Z*) : 47 (*E* / *Z*)
PhSH, 60 °C, 1.5 h	88%	20 (15/1) : 1 (5/2)
Ph_3SnH-Et_3B, r.t., 0.5 h	74%	16 (15/1) : 1 (2/1)



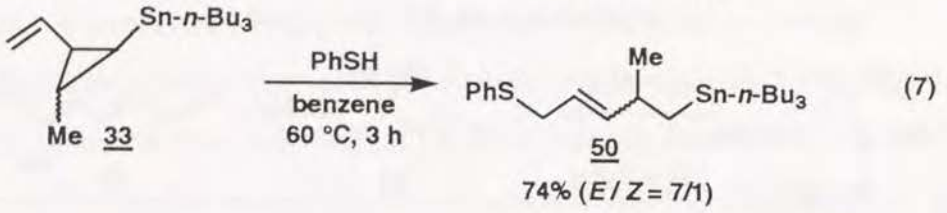
(5)

Reaction conditions	Yield
PhSH, 60 °C, 3 h	45%
Ph_3SnH-Et_3B, r.t., 0.5 h	65%

Treatment of stannylcyclopropanes **31** and **33** with benzenethiol also provided homoallylic stannanes exclusively (eq 6 and 7).



(6)



(7)

Experimental

Analytical TLC was performed on commercial glass plates bearing a 0.25 mm layer of Merck silica gel PF254. The TLC mobility of a given component is described by its R_f value, the ratio of the distance moved by that component to the distance moved by the solvent front. PLC plates were prepared as follows: a free-flowing slurry of Merck silica gel PF254 (25 g) in water (60 ml) was spread on a clean glass plate (20 x 20 cm) to an even depth of 1.5 mm and the plate was air-dried at room temperature for at least two days before use. Analytical and preparative GLPC were performed with a Shimadzu Gas Chromatograph, Model GC-8A using thermal conductivity detector and helium as carrier gas (3.0 kg/cm^2). Product percentages were calculated from peak area ratios without correction for detector response. Two columns (OV-1 2%, 2 m on Chromosorb W 60-80 mesh AW DMCS (Column A) and SE-30 1.5%, 2 m on Chromosorb W 60-80 mesh AW DMCS (Column B)) were used. LC was performed with Japan Analytical Industry Co. Ltd. LC-908 (Column: JAIGEL 1-H and 2-H) using chloroform at a flow rate of 4 ml/min. The GLPC and LC retention time (t_r) of a component denotes the time (in minutes) at which the maximum concentration of that component reached the detector.

(*Z*)-3-Dimethylphenylsilyl-2-propen-1-ol (1). *i*-Bu$_2$AlH (6.6 ml, 37 mmol) was added dropwise to a solution of tetrahydropyranyl ether of 3-dimethylphenylsilyl-2-propyn-1-ol (8.6 g, 31 mmol) in hexane (30 ml) at 0 °C. After stirring for 10 h at room temperature, the reaction mixture was poured into 1 M aqueous HCl (70 ml). The product was extracted with hexane (50 ml x 2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residual oil was dissolved in MeOH (50 ml) and *p*-TsOH (100 mg) was added. The resulting mixture was stirred for 2 h at room temperature. Et_3N (1 ml) was added

and stirring of the mixture was continued for another 5 min. The mixture was concentrated *in vacuo* and crude product was purified by silica-gel column chromatography (hexane/AcOEt = 5/1) to give the title alcohol in 86% yield (5.1 g).

***cis*-1-Dimethylphenylsilyl-2-hydroxymethylcyclopropane (2).** According to the reported procedure,[9] CH_2I_2 (2.2 ml, 7.3 g, 27 mmol) was added dropwise over 20 min to a mixture of allylic alcohol **1** (2.5 g, 13 mmol), Et_2Zn (2 ml, 20 mmol), and *i*-Pr_2O (15 ml) under argon atmosphere at room temperature. Exothermic reaction occurred. Stirring was continued for 30 min after completion of the addition. The resulting mixture was poured slowly into 1 M HCl solution and the product was extracted with AcOEt. The organic layer was washed with 10% aqueous $Na_2S_2O_3$ and dried over anhydrous Na_2SO_4. Purification by silica-gel column chromatography (hexane/AcOEt = 5/1) gave the title compound in 60% yield (1.57 g): Bp 74 °C (1 Torr, bath temp); IR (neat) 3322, 3064, 2994, 2952, 1427. 1412, 1292, 1248, 1112, 1036, 1015, 939, 889, 864, 832, 814, 771, 730, 699, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (ddd, *J*=9.9, 9.3, 7.6 Hz, 1H), 0.27–0.35 (m, 1H), 0.32 (s, 6H), 0.95 (ddd, *J*=9.9, 7.9, 3.8 Hz, 1H), 1.15 (bs, 1H), 1.40 (ddtd, *J*=9.3, 7.9, 7.6, 5.0 Hz, 1H), 3.40 (bs, 2H), 7.35–7.40 (m, 3H), 7.55–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -1.88, -1.19, 1.77, 7.72, 19.51, 65.23, 127.9, 129.1, 133.6, 139.6. Found: C, 69.80; H, 9.09%. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%.

***cis*-1-Dimethylphenylsilyl-2-vinylcyclopropane (3).** DMSO (1.38 ml, 19.5 mmol) in CH_2Cl_2 (3 ml) was added dropwise over 5 min at -78 °C to a mixture of $(COCl)_2$ (0.85 ml, 9.8 mmol) and CH_2Cl_2 (10 ml). After stirring for 15 min, a solution of **2** (1.34 g, 6.5 mmol) in CH_2Cl_2 (10 ml) was added over 10 min. The reaction mixture was stirred for 30 min and then Et_3N (5.4 ml, 39 mmol) was added. After 5 min, dry ice-MeOH cooling bath was removed and H_2O (50 ml) was added to the resulting white suspension. Instantly the solid dissolved and clear solution was obtained. The mixture was extracted with CH_2Cl_2 (50 ml x 2) and the

combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. A THF solution of crude aldehyde (1.3 g) was added to a suspension of $Ph_3P=CH_2$ prepared from Ph_3PCH_3I (3.5 g, 8.5 mmol) and *t*-BuOK (0.95 g, 8.5 mmol) in THF (25 ml) at 0 °C and the resultant mixture was stirred for 1 h at room temperature. The mixture was poured into saturated aqueous NH_4Cl (50 ml) and extracted with hexane (50 ml x 2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to 20 ml to afford triphenylphosphine oxide as white precipitate. The white solid was filtered off and the filtrate was concentrated again. Purification of the residual crude product by silica-gel column chromatography gave vinylcyclopropane **3** in 89% yield (1.17 g) from **2**: Bp 52 °C (1 Torr, bath temp); IR (neat) 3066, 2994, 2952, 1637, 1428, 1286, 1248, 1112, 1040, 989, 961, 937, 895, 847, 830, 812, 772, 728, 699, 668, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 (ddd, *J*=10.1, 9.7, 8.0 Hz, 1H), 0.29 (s, 6H), 0.54 (ddd, *J*=8.0, 4.9, 3.9 Hz, 1H), 1.10 (ddd, *J*=10.1, 7.7, 3.9 Hz, 1H), 1.79 (dddd, *J*=9.7, 9.0, 7.7, 4.9 Hz, 1H), 4.88 (dd, *J*=9.9, 2.2 Hz, 1H), 5.12 (dd, *J*=16.9, 2.2 Hz, 1H), 5.41 (ddd, *J*=16.9, 9.7, 9.0 Hz, 1H), 7.33–7.42 (m, 3H), 7.55–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -1.75, -1.69, 5.26, 10.75, 20.58, 113.5, 127.7, 128.8, 133.8, 139.7, 140.8. Found: C, 77.22; H, 8.91%. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97%.

***(E)*-3-Dimethylphenylsilyl-2-propen-1-ol (4).** The title compound (9.4 g, 87% yield) was prepared by the reduction of 3-dimethylphenylsilyl-2-propyn-1-ol (10.7 g, 56.2 mmol) with sodium bis(2-methoxyethoxy)aluminum hydride (70% toluene solution, 26.7 ml) following the procedure for the synthesis of (*E*)-3-trimethylsilyl-2-propen-1-ol.[17]

***trans*-1-Dimethylphenylsilyl-2-hydroxymethylcyclopropane (5).** In similar fashion to the synthesis of **2**, treatment of alcohol **4** (3.13 g, 16.3 mmol) with CH_2I_2 (2.7 ml, 9.0 g, 33.5 mmol) and Et_2Zn (2.5 ml, 25 mmol) in *i*-Pr_2O (18 ml) gave cyclopropane **5** in 76% yield (2.56 g): Bp 79 °C (1 Torr, bath temp); IR

(neat) 3316, 3064, 2994, 2952, 2864, 1428, 1411, 1302, 1249, 1114, 1054, 1020, 942, 865, 831, 813, 771, 728, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.28 (ddd, *J*=9.9, 7.0, 6.4 Hz, 1H), 0.21 (s, 3H), 0.22 (s, 3H), 0.48–0.60 (m, 2H), 0.99–1.15 (m, 1H), 1.39 (bs, 1H), 3.46 (dd, *J*=14.4, 6.6 Hz, 1H), 3.52 (dd, *J*=14.4, 6.9 Hz, 1H), 7.34–7.39 (m, 3H), 7.53–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -3.90, 1.37, 7.22, 18.11, 68.46, 127.7, 129.0, 133.7, 138.6. Found: C, 69.58; H, 8.85%. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%.

***trans*-1-Dimethylphenylsilyl-2-vinylcyclopropane (6).** The compound (2.04 g, 81% yield) was prepared from **5** (2.56 g) following the procedure described for the synthesis of **3**: Bp 54 °C (1 Torr, bath temp); IR (neat) 3066, 2994, 2954, 1636, 1428, 1249, 1115, 1087, 1062, 985, 969, 947, 892, 831, 817, 772, 728, 698, 655 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.06 (ddd, *J*=10.0, 7.6, 6.1 Hz, 1H), 0.20 (s, 3H), 0.21 (s, 3H), 0.65–0.78 (m, 2H), 1.39 (dddd, *J*=8.5, 7.2, 6.1, 4.9 Hz, 1H), 4.85 (dd, *J*=10.0, 2.0 Hz, 1H), 5.09 (dd, *J*=17.0, 2.0 Hz, 1H), 5.36 (ddd, *J*=17.0, 10.0, 8.5 Hz, 1H), 7.33–7.38 (m, 3H), 7.52–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -3.83, -3.77, 5.62, 10.73, 19.37, 111.4, 127.7, 128.9, 133.8, 138.7, 143.1. Found: C, 77.10; H, 9.22%. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97%.

***r*-1-Dimethylphenylsilyl-*c*-2-hydroxymethyl-*t*-3-methylcyclopropane (*trans*-7) and *r*-1-Dimethylphenylsilyl-*c*-2-hydroxymethyl-*c*-3-methylcyclopropane (*cis*-7).** A solution of CH_3CHI_2 (2.8 ml, 28 mmol) in *i*-Pr_2O (5 ml) was added dropwise over 1 h to a mixture of allylic alcohol **1** (1.90 g, 9.4 mmol), Et_2Zn (2.8 ml, 28 mmol), and *i*-Pr_2O (13 ml) under argon atmosphere at room temperature. Exothermic reaction proceeded gradually. After stirring for 12 h, the reaction mixture was poured into 1 M HCl (50 ml) and the product was extracted with AcOEt (50 ml x 2). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by silica-gel column chromatography gave the title compounds (1.22 g, 59% yield) which was contaminated by

the starting allylic alcohol **1**. ^1H NMR spectrum showed that the ratio between products (two isomers) and **1** was 4.6:1. The analytical pure samples of both isomers were prepared by preparative GLPC (Column B, 150 °C, t_r=4.67 min (***trans*-7**) and 6.35 min (***cis*-7**), ***trans*-7**/***cis*-7** = 25/1). ***trans*-7**: Bp 77 °C (1 Torr, bath temp); IR (neat) 3318, 3064, 2990, 2948, 2862, 1458, 1448, 1428, 1380, 1249, 1113, 1077, 1018, 991, 941, 924, 832, 817, 773, 728, 699, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ - 0.25 (dd, *J*=9.2, 6.9 Hz, 1H), 0.30 (s, 3H), 0.31 (s, 3H), 0.69–0.83 (m, 1H), 1.03–1.15 (m, 2H), 1.18 (d, 3H), 3.34 (dd, *J*=11.4, 7.5 Hz, 1H), 3.48 (dd, *J*=11.4, 7.5 Hz, 1H), 7.34–7.39 (m, 3H), 7.54–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ - 1.67, -0.91, 11.29, 16.70, 20.46, 28.46, 65.07, 127.9, 129.0, 133.6, 139.8. Found: C, 70.69; H, 9.38%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%. ***cis*-7**: Bp 79 °C (1 Torr, bath temp); IR (neat) 3316, 3064, 3046, 2996, 2950, 1459, 1450, 1427, 1407, 1389, 1288, 1249, 1111, 1074, 1057, 1018, 939, 914, 834, 816, 773, 728, 699, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (t, *J*=9.6 Hz, 1H), 0.37 (s, 6H), 1.14 (d, *J*=6.3 Hz, 3H), 1.17–1.54 (m, 3H), 3.61 (dd, *J*=11.3, 8.1 Hz, 1H), 3.70 (dd, *J*=11.3, 6.9 Hz, 1H), 7.33–7.38 (m, 3H), 7.56–7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.23, 7.72, 11.82, 14.80, 23.12, 61.48, 127.8, 128.9, 133.5, 140.3. Found: C, 70.62; H, 9.37%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

r*-1-Dimethylphenylsilyl-*c*-2-formyl-*t*-3-methylcyclopropane (*trans*-8) and *r*-1-Dimethylphenylsilyl-*c*-2-formyl-*c*-3-methylcyclopropane (*cis*-8).** The mixture of **7** (1.22 g, 5.54 mmol) and **1** (0.26 g, 1.35 mmol) was oxidized with $(COCl)_2$ (0.90 ml, 10.3 mmol), DMSO (1.46 ml, 20.6 mmol), and Et_3N (5.72 ml, 41.7 mmol) (Swern oxidation) following the procedure described for the synthesis of **3**. Purification of crude product by silica-gel column chromatography gave pure aldehyde **8** (trans*-8**/***cis*-8** = 20/1) in 81% yield (0.98 g). Careful separation by PLC (R_f=0.48 (***trans*-8**) and 0.43 (***cis*-8**), hexane/AcOEt = 10/1) gave the analytical pure samples. ***trans*-8**: Bp 68 °C (1 Torr, bath temp); IR (neat) 3066,

3046, 2996, 2952, 2924, 2864, 2820, 2730, 1707, 1459, 1428, 1412, 1252, 1179, 1111, 1076, 952, 923, 863, 833, 818, 781, 731, 701, 667 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.36 (s, 3H), 0.37 (s, 3H), 0.45 (dd, *J*=9.4, 8.8 Hz, 1H), 1.25 (d, *J*=5.8 Hz, 3H), 1.60 (dqd, *J*=8.8, 5.8, 4.1 Hz, 1H), 1.77 (ddd, *J*=9.4, 6.8, 4.1 Hz, 1H), 7.35–7.42 (m, 3H), 7.51–7.57 (m, 2H), 8.88 (d, *J*=6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.68, 18.96, 19.54, 21.47, 37.79, 128.0, 129.3, 133.6, 138.2, 201.2. Found: C, 71.45; H, 8.52%. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31%. ***cis*-8**: Bp 70 °C (1 Torr, bath temp); IR (neat) 3066, 3046, 3006, 2952, 2846, 2758, 2724, 1701, 1648, 1458, 1452, 1428, 1389, 1375, 1289, 1251, 1173, 1112, 1068, 998, 942, 895, 869, 834, 816, 778, 732, 699, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.44 (s, 3H), 0.47 (s, 3H), 0.73 (t, *J*=9.6 Hz, 1H), 1.33 (d, *J*=6.5 Hz, 3H), 1.92 (ddq, *J*=9.6, 8.1, 6.5 Hz, 1H), 2.08 (ddd, *J*=9.6, 8.1, 6.4 Hz, 1H), 7.35–7.40 (m, 3H), 7.54–7.60 (m, 2H), 9.36 (d, *J*=6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -0.33, 0.07, 12.51, 16.53, 22.84, 32.62, 127.9, 129.2, 133.6, 139.2, 202.7. Found: C, 71.51; H, 8.34%. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31%.

r*-1-Dimethylphenylsilyl-*t*-3-methyl-*c*-2-vinylcyclopropane (*trans*-9) and *r*-1-Dimethylphenylsilyl-*c*-3-methyl-*c*-2-vinylcyclopropane (*cis*-9).** Wittig reaction (Ph_3PCH_3I (2.1 g, 5.2 mmol) and *t*-BuOK (0.58 g, 5.2 mmol)) of **8** (trans*-8/*cis*-8** = 20/1, 0.87 g, 4.0 mmol) followed by purification by silica-gel column chromatography gave the title compound **9** in 90% yield (0.78 g, ***trans*-9/*cis*-9** = 17/1). Analytical samples were prepared by preparative GLPC (Column A, 150 °C, t_r=3.55 min (***trans*-9**) and 4.28 min (***cis*-9**)). ***trans*-9**: Bp 53 °C (1 Torr, bath temp); IR (neat) 3066, 3048, 2992, 2948, 2922, 2896, 2862, 1635, 1459, 1428, 1376, 1249, 1113, 1073, 981, 950, 925, 893, 832, 811, 770, 728, 700, 676, 661 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.09 (dd, *J*=9.6, 7.4 Hz, 1H), 0.27 (s, 6H), 0.93 (dqd, *J*=7.4, 5.7, 4.4 Hz, 1H), 1.18 (d, *J*=5.7 Hz, 3H), 1.47 (td, *J*=9.6, 4.4 Hz, 1H), 4.85 (dd, *J*=9.9, 2.2 Hz, 1H), 5.09 (dd, *J*=17.0, 2.2 Hz, 1H), 5.41 (ddd, *J*=17.0,

9.9, 9.6 Hz, 1H), 7.34–7.40 (m, 3H), 7.54–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -1.57, -1.46, 14.96, 19.50, 20.30, 29.74, 112.9, 127.7, 128.7, 133.8, 140.0, 140.7. Found: C, 77.76; H, 9.49%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%. ***cis*-9**: Bp 51 °C (1 Torr, bath temp); IR (neat) 3066, 3048, 2996, 2952, 2924, 2872, 2852, 1631, 1428, 1286, 1259, 1249, 1112, 1070, 1017, 992, 920, 895, 833, 818, 775, 728, 698, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (t, *J*=9.7 Hz, 1H), 0.34 (s, 3H), 0.37 (s, 3H), 1.14 (d, *J*=6.5 Hz, 3H), 1.47 (ddq, *J*=9.7, 8.3, 6.5 Hz, 1H), 1.90 (ddd, *J*=9.9, 9.7, 8.3 Hz, 1H), 5.00 (ddd, *J*=10.2, 2.2, 0.6 Hz, 1H), 5.22 (ddd, *J*=16.8, 2.2, 0.6 Hz, 1H), 5.68 (ddd, *J*=16.8, 10.2, 9.9 Hz, 1H), 7.32–7.37 (m, 3H), 7.54–7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.12, 0.19, 11.67, 12.61, 17.50, 25.12, 114.5, 127.7, 128.7, 133.7, 137.6, 140.6. Found: C, 77.59; H, 9.29%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%.

r*-1-Dimethylphenylsilyl-*t*-2-hydroxymethyl-*c,t*-3-methylcyclopropane (10).** Cyclopropanation of **4** (2.0 g, 10.4 mmol) with CH_3CHI_2 (2 ml, 20 mmol) and Et_2Zn (2 ml, 20 mmol) gave the cyclopropane **10** (0.53 g, 23% yield) which was contaminated by **4** (0.90 g, 46% recovery). **10** (cis*-10/*trans*-10** = 36/64) was separated from **4** by preparative GLPC: Bp 75 °C (1 Torr, bath temp); IR (neat) 3316, 3064, 3046, 2992, 2950, 2870, 1458, 1449, 1428, 1382, 1248, 1113, 1072, 1021, 949, 924, 817, 773, 728, 698, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.54 (t, *J*=6.7 Hz, 0.64H), -0.26 (t, *J*=8.0 Hz, 0.36H), 0.20 (s, 3.84H), 0.30 (s, 1.08H), 0.32 (s, 1.08H), 0.89–1.40 (m, 6H), 3.45–3.61 (m, 1.36H), 3.77 (dd, *J*=11.2, 6.1 Hz, 0.64H), 7.34–7.40 (m, 3H), 7.51–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -3.68, -1.19, -1.15, 8.66, 10.20, 14.11, 14.46, 16.47, 17.17, 22.69, 27.14, 63.63, 68.56, 127.8, 128.8, 128.9, 133.6, 139.0, 139.9. Found: C, 71.12; H, 9.39%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

***r*-1-Dimethylphenylsilyl-*t*-2-formyl-*t*-3-methylcyclopropane (*trans*-11) and *r*-1-Dimethylphenylsilyl-*t*-2-formyl-*c*-3-methylcyclopropane (*cis*-11).**

The mixture of **4** (4.8 mmol) and **10** (2.4 mmol) was treated with $(COCl)_2$ (0.94 ml, 10.8 mmol), DMSO (1.53 ml, 21.6 mmol) and Et_3N (6.0 ml, 43.2 mmol) to give the title compound in 50% yield (0.26 g, 1.2 mmol, ***trans*-11**/***cis*-11** = 2/1). PLC separation of isomers (R_f=0.41 (***trans*-11**) and 0.34 (***cis*-11**), hexane/AcOEt = 10/1) provided the analytical samples. ***trans*-11**: Bp 67 °C (1 Torr, bath temp); IR (neat) 3066, 3046, 2996, 2952, 2874, 2822, 2746, 2718, 1701, 1655, 1647, 1459, 1428, 1396, 1379, 1251, 1171, 1115, 1073, 1017, 997, 954, 928, 881, 834, 780, 731, 700, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 3H), 0.27 (s, 3H), 0.80 (dd, *J*=7.7, 6.4 Hz, 1H), 1.32–1.53 (m, 4H), 1.75 (dt, *J*=7.7, 5.9 Hz, 1H), 7.34–7.41 (m, 3H), 7.47–7.53 (m, 2H), 9.28 (d, *J*=5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -4.07, -3.77, 14.51, 16.40, 21.98, 32.00, 127.9, 129.4, 133.6, 137.0, 201.4. Found: C, 71.28; H, 8.45%. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31%. ***cis*-11**: Bp 67 °C (1 Torr, bath temp); IR (neat) 3066, 3046, 2994, 2954, 2816, 2718, 1709, 1459, 1428, 1412, 1251, 1206, 1173, 1115, 1085, 1068, 1022, 1005, 935, 874, 834, 815, 777, 731, 701, 666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.36 (s, 3H), 0.37 (s, 3H), 0.77 (dd, *J*=10.4, 6.3 Hz, 1H), 1.12 (d, *J*=6.2 Hz, 3H), 1.65 (ddd, *J*=6.3, 6.1, 3.9 Hz, 1H), 1.75 (ddq, *J*=10.4, 6.2, 3.9 Hz, 1H), 7.35–7.41 (m, 3H), 7.50–7.57 (m, 2H), 8.77 (d, *J*=6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.78, -1.53, 13.75, 15.34, 20.74, 35.77, 127.9, 129.3, 133.6, 138.0, 201.0. Found: C, 71.51; H, 8.34%. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31%.

r*-1-Dimethylphenylsilyl-*t*-3-methyl-*t*-2-vinylcyclopropane (*trans*-12) and *r*-1-Dimethylphenylsilyl-*c*-3-methyl-*t*-2-vinylcyclopropane (*cis*-12).** Wittig reaction (Ph_3PCH_3I (0.67 g, 1.67 mmol) and *t*-BuOK (0.19 g, 1.67 mmol)) of **11** (0.26 g, 1.2 mmol) gave **12** in 74% yield (0.19 g, ***trans*-12**/cis*-12** = 2/1). Each pure sample was prepared by PLC (R_f=0.62 (***trans*-12**) and R_f=0.60 (***cis*-12**), hexane). ***trans*-12**: Bp 57 °C (1 Torr, bath temp); IR (neat) 3066, 3046, 2994, 2952, 2926, 2900, 2868, 1633, 1459, 1428, 1249, 1115, 1090, 1071, 990, 961, 929, 894, 835, 780, 729, 698, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.27 (t, *J*=6.7 Hz, 1H), 0.20 (s, 6H), 1.02 (ddq, *J*=8,7, 6.7, 5.8 Hz, 1H), 1.14 (d, *J*=5.8 Hz, 3H), 1.47 (td, *J*=8.7, 6.7 Hz, 1H), 4.98 (dd, *J*=10.1, 2.0 Hz, 1H), 5.12 (dd, *J*=17.0, 2.0 Hz, 1H), 5.63 (ddd, *J*=17.0, 10.1, 8.7 Hz, 1H), 7.32–7.39 (m, 3H), 7.50–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -3.54, 13.69, 14.85, 17.00, 24.67, 113.7, 127.7, 128.9, 133.8, 138.7, 139.1. Found: C, 77.76; H, 9.38%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%. ***cis*-12**: Bp 57 °C (1 Torr, bath temp); IR (neat) 3066, 3048, 2994, 2950, 2868, 1635, 1459, 1450, 1428, 1410, 1249, 1113, 1069, 1015, 980, 927, 891, 835, 811, 795, 783, 768, 728, 699, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (dd, *J*=9.6, 6.6 Hz, 1H), 0.28 (s, 3H), 0.31 (s, 3H), 1.02–1.29 (m, 5H), 4.82 (dd, *J*=10.0, 1.7 Hz, 1H), 5.05 (dd, *J*=17.1, 1.7 Hz, 1H), 5.39 (ddd, *J*=17.1, 10.0, 8.5 Hz, 1H), 7.31–7.38 (m, 3H), 7.50–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -1.37, -0.91, 13.09, 16.37, 20.53, 28.61, 111.0, 127.7, 128.8, 133.7, 140.0, 143.4. Found: C, 78.01; H, 9.49%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%.

(2,2-Dibromo-*trans*-3-methylcyclopropyl)methyl 2-tetrahydropyranyl ether (13). Tetrahydropyranyl ether of 2-buten-1-ol (15.7 g, 100 mmol) was added to a mixture of hexane (150 ml) and *t*-BuOK (22.5 g, 200 mmol) at -20 °C under argon atmosphere. Then, $CHBr_3$ (17.5 ml, 200 mmol) was added dropwise to the solution over 1.5 h from dropping funnel. After stirring at -20 °C for 2 h and at room temperature for 10 h, reaction mixture was poured into saturated aqueous NaCl (200 ml). The organic layer was removed and the aqueous layer was extracted with hexane (200 ml). The combined organic layer was dried over anhydrous Na_2SO_4. Concentration and successive purification by silica-gel column chromatography (hexane/AcOEt = 20/1) gave **13** in 70% yield (diastereomeric mixture, 23.0 g): Bp 80 °C (dec, 1 Torr, bath temp); IR (neat) 2938, 2868, 1466, 1453, 1382, 1350, 1262, 1202, 1184, 1158, 1133, 1121, 1059, 1033, 991, 965, 943, 905, 869, 814, 743, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15–1.89 (m, 11H), 3.49–3.64 (m, 2H),

3.78–3.96 (m, 2H), 4.69 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 16.90, 19.13, 19.41, 25.38, 29.89, 30.46, 30.62, 36.26, 36.70, 61.99, 62.28, 68.95, 69.38, 98.37, 98.94. Found: C, 36.82; H, 4.98%. Calcd for $C_{10}H_{16}O_2Br_2$: C, 36.61; H, 4.92%.

***t*-2-Hydroxymethyl-*c*-3-methyl-*r*-1-trimethylsilylcyclopropane (*trans*-14) and *c*-2-Hydroxymethyl-*t*-3-methyl-*r*-1-trimethylsilylcyclopropane (*cis*-14).** A hexane solution of *n*-BuLi (1.6 M, 34 ml, 54 mmol) was added dropwise over 20 min from dropping funnel to a THF (100 ml) solution of **13** (17 g, 52 mmol) and Me_3SiCl (33 ml, 260 mmol) at -107 °C (isooctane-liq. N_2) under argon atmosphere. After stirring for 2 h, cooling bath was removed and the mixture was stirred for another 20 min. The mixture was slowly poured into saturated aqueous $NaHCO_3$ (200 ml). The product was extracted with AcOEt (150 ml x 2) and the extracts were dried and concentrated *in vacuo*. The residual oil was dissolved in benzene (100 ml) and *n*-Bu_3SnH (17.5 g, 60 mmol) was added to the solution under argon atmosphere. A hexane solution of Et_3B (1.0 M, 3.0 ml, 3.0 mmol) was added to the mixture at room temperature and exothermic reaction occurred instantly. After stirring for 1 h, CH_2Cl_2 (200 ml), KF (35 g), and water (11 ml) were added and the resulting mixture was stirred for 12 h. The precipitate was filtered by glass filter and the filtrate was concentrated *in vacuo*. The crude product was dissolved into methanol (150 ml) and *p*-TsOH-H_2O (1.0 g) was added. After stirring for 2 h, Et_3N (3 ml) was added and the reaction mixture was concentrated. Purification of the product by silica-gel column chromatography (hexane/AcOEt = 10/1) gave **14** in 71% yield (5.73 g, ***trans*-14/*cis*-14** = 64/36). The isomers were separated each other by PLC. ***trans*-14**: Bp 95 °C (27 Torr, bath temp); IR (neat) 3322, 2988, 2950, 2868, 1458, 1406, 1249, 1086, 1020, 990, 948, 926, 854, 835, 755, 687, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.49 (dd, *J*=9.5, 6.8 Hz, 1H), 0.04 (s, 9H), 0.80–1.00 (m, 2H), 1.10 (d, *J*=5.8 Hz, 3H), 1.54 (bs, 1H), 3.46 (d, *J*=6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -0.10, 9.21, 16.44, 16.95, 26.89, 68.64.

Found: C, 60.88; H, 11.64%. Calcd for $C_8H_{18}OSi$: C, 60.69; H, 11.46%. ***cis*-14**: Bp 100 °C (27 Torr, bath temp); IR (neat) 3328, 2990, 2950, 2898, 2866, 1462, 1448, 1380, 1249, 1076, 1021, 992, 944, 924, 837, 757, 688, 662 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.50 (dd, *J*=9.4, 7.0 Hz, 1H), 0.03 (s, 9H), 0.67 (dqd, *J*=7.0, 5.8, 4.2 Hz, 1H), 1.07 (dddd, *J*=9.4, 7.9, 7.3, 4.2 Hz, 1H), 1.14 (d, *J*=5.8 Hz, 3H), 1.44 (bs, 1H), 3.47 (dd, *J*=11.0, 7.9 Hz, 1H), 3.56 (dd, *J*=11.0, 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -0.05, 11.99, 16.50, 20.58, 28.34, 65.28. Found: C, 60.68; H, 11.68%. Calcd for $C_8H_{18}OSi$: C, 60.69; H, 11.46%.

***c*-3-Methyl-*r*-1-trimethylsilyl-*t*-2-vinylcyclopropane and *t*-3-Methyl-*r*-1-trimethylsilyl-*c*-2-vinylcyclopropane (74:26) (15).** Swern oxidation and successive Wittig reaction provided vinylcyclopropane **15** in 53% overall yield from **14**: Bp 70–72 °C (55 Torr); IR (neat) 3078, 2994, 2950, 2896, 2868, 1635, 1459, 1375, 1289, 1249, 1090, 1069, 980, 950, 927, 891, 837, 793, 748, 688, 657, 636 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.31 (dd, *J*=9.5, 7.2 Hz, 0.26H), -0.22 (dd, *J*=9.3, 6.8 Hz, 0.74H), 0.02 (s, 2.34H), 0.06 (s, 6.66H), 0.78–0.99 (m, 0.26H), 1.00–1.27 (m, 4.48H), 1.41 (td, *J*=10.0, 4.5 Hz, 0.26H), 4.79 (dd, *J*=10.0, 1.9 Hz, 0.74H), 4.87 (dd, *J*=10.0, 2.2 Hz, 0.26H), 5.02 (dd, *J*=17.2, 1.9 Hz, 0.74H), 5.09 (dd, *J*=16.8, 2.2 Hz, 0.26H), 5.37 (ddd, *J*=17.2, 10.0, 8.3 Hz, 0.74H), 5.46 (dt, *J*=16.8, 10.0 Hz, 0.26H); ^{13}C NMR ($CDCl_3$) δ -0.29, 0.00, 14.08, 15.93, 16.36, 19.36, 20.44, 28.39, 29.65, 110.4, 112.4, 141.1, 143.9. Found: C, 69.80; H, 11.92%. Calcd for $C_9H_{18}Si$: C, 70.05; H, 11.76%.

2,2-Dibromo-3,3-dimethylcyclopropylmethyl 2-tetrahydropyranyl ether (16). An addition of dibromocarbene ($CHBr_3$, *t*-BuOK) to prenyl alcohol tetrahydropyranyl ether gave cyclopropane **16** (diastereomeric mixture) in 81% yield: Bp 85 °C (dec, 1 Torr, bath temp); IR (neat) 2938, 2868, 1455, 1441, 1374, 1353, 1342, 1322, 1284, 1274, 1262, 1201, 1183, 1158, 1134, 1121, 1079, 1059, 1031, 979, 906, 869, 815, 755, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 3H), 1.43 (s,

3H), 1.50–1.98 (m, 7H), 3.44–4.01 (m, 4H), 4.64–4.71 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 19.14, 19.34, 19.47, 25.35, 27.16, 28.38, 30.51, 30.57, 38.24, 38.43, 44.63, 44.81, 61.94, 62.16, 66.08, 66.21, 98.45, 98.85. Found: C, 38.53; H, 5.26%. Calcd for $C_{11}H_{18}O_2Br_2$: C, 38.62; H, 5.30%.

2-Bromo-3,3-dimethyl-2-trimethylsilylcyclopropylmethyl tetrahydropyranyl ether (17, *cis trans* mixture). According to the description for the synthesis of **14**, the title compound was obtained in 65% yield (8.5 g) starting from **16** (13.3 g, 39 mmol): Bp 82 °C (dec, 1 Torr, bath temp); IR (neat) 2942, 2868, 1456, 1442, 1408, 1384, 1373, 1342, 1322, 1284, 1249, 1201, 1184, 1160, 1134, 1119, 1078, 1056, 1029, 997, 974, 951, 929, 904, 841, 815, 763, 735, 682, 628 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19–0.27 (m, 9H), 0.90–1.28 (m, 4H), 1.43–1.95 (m, 9H), 3.40–3.65 (m, 2H), 3.72–4.03 (m, 2H), 4.64 (bs, 1H). Found: C, 50.23; H, 8.39%. Calcd for $C_{14}H_{27}O_2SiBr$: C, 50.14; H, 8.12%.

trans*-2-Hydroxymethyl-3,3-dimethyl-1-trimethylsilylcyclopropane (*trans*-18) and *cis*-2-Hydroxymethyl-3,3-dimethyl-1-trimethylsilylcyclopropane (*cis*-18).** Hydrodebromination of **17** was performed by two methods. Procedure A: Reduction with *n*-Bu_3SnH (3.33 g, 11.4 mmol)-Et_3B (1.0 M hexane solution, 1 ml) system as described for the synthesis of **14** followed by deprotection of tetrahydropyranyl ether (*p*-TsOH-MeOH) gave **18** in 90% yield (1.61 g, ***cis*-18**/trans*-18** = 3.8/1) starting from **17** (3.49 g, 10.4 mmol). Procedure B: *n*-BuLi (1.54 M hexane solution, 7.9 ml, 12.2 mmol) was added over 5 min to a solution of **17** (3.73 g, 11.1 mmol) in THF (22 ml) at -78 °C. After stirring for 1 h, AcOH (1.4 ml, 24 mmol) was added to the reaction mixture and then cooling bath was removed. After stirring for additional 15 min at room temperature, the resulting mixture was poured into saturated aqueous $NaHCO_3$ (50 ml) and the product was extracted with AcOEt (50 ml x 2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Deprotection of tetrahydropyranyl ether

followed by purification by silica-gel column chromatography (hexane/AcOEt = 10/1) gave **18** in 62% yield (1.19 g, ***trans*-18**/***cis*-18** = 11/1). Analytical pure samples were prepared by preparative GLPC (Column B, 130 °C, t_r=8.37 min (***trans*-18**) and 9.46 min (***cis*-18**)). ***trans*-18**: Bp 52 °C (1 Torr, bath temp); IR (neat) 3314, 2948, 2870, 1454, 1412, 1376, 1300, 1248, 1120, 1083, 1049, 1016, 964, 953, 926, 865, 835, 760, 687, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.67 (d, *J*=7.2 Hz, 1H), 0.02 (s, 9H), 0.96 (ddd, *J*=8.3, 7.2, 6.3 Hz, 1H), 1.12 (s, 3H), 1.16 (s, 3H), 1.28 (bs, 1H), 3.53 (dd, *J*=11.4, 8.3 Hz, 1H), 3.72 (dd, *J*=11.4, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -0.17, 17.86, 21.90, 22.77, 25.14, 31.78, 64.98. Found: C, 62.83; H, 11.91%. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70%. ***cis*-18**: Bp 50 °C (1 Torr, bath temp); IR (neat) 3308, 2948, 2890, 1453, 1412, 1375, 1290, 1248, 1120, 1045, 1018, 966, 938, 835, 757, 685, 655 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.36 (d, *J*=9.9 Hz, 1H), 0.07 (s, 9H), 1.12–1.26 (m, 8H), 3.61 (dd, *J*=11.2, 8.7 Hz, 1H), 3.72 (dd, *J*=11.2, 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.13, 17.55, 18.17, 21.09, 30.81, 32.07, 62.39. Found: C, 62.45; H, 11.97%. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70%.

trans*-3,3-Dimethyl-1-trimethylsilyl-2-vinylcyclopropane (*trans*-19) and *cis*-3,3-Dimethyl-1-trimethylsilyl-2-vinylcyclo-propane (*cis*-19).** According to the synthesis of **3**, Swern oxidation and Wittig reaction of **18** (*cis*-rich) or **18** (*trans*-rich) gave **19** (*cis*-rich) or **19** (*trans*-rich) in 57% or 51% yield, respectively. Analytical samples were obtained by preparative GLPC (Column B, 50 °C, t_r=6.78 min (trans*-19**) and 8.09 min (***cis*-19**)). ***trans*-19**: Bp 63 °C (40 Torr, bath temp); IR (neat) 3078, 2948, 2868, 1634, 1458, 1375, 1248, 1133, 1117, 982, 909, 892, 860, 836, 768, 752, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.38 (d, *J*=7.0 Hz, 1H), 0.03 (s, 9H), 1.11 (s, 6H), 1.31 (dd, *J*=8.7, 7.0 Hz, 1H), 4.92 (dd, *J*=10.0, 2.1 Hz, 1H), 5.06 (dd, *J*=17.0, 2.1 Hz, 1H), 5.62 (ddd, *J*=17.0, 10.0, 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -0.14, 21.69, 23.60, 24.24, 24.82, 33.86, 112.8, 140.4. Found: C, 71.23; H, 12.20%. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97%. ***cis*-19**:

Bp 58 °C (40 Torr, bath temp); IR (neat) 3078, 2950, 1632, 1457, 1375, 1248, 1118, 984, 920, 894, 836, 765, 754, 722, 686, 653 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.17 (d, *J*=9.9 Hz, 1H), 0.07 (s, 9H), 1.13 (s, 3H), 1.15 (s, 3H), 1.58 (t, *J*=9.9 Hz, 1H), 4.94 (dd, *J*=10.2, 2.2 Hz, 1H), 5.14 (dd, *J*=16.9, 2.2 Hz, 1H), 5.66 (ddd, *J*=16.9, 10.2, 9.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.00, 19.06, 21.62, 23.59, 30.58, 34.20, 113.5, 138.6. Found: C, 71.12; H, 12.20%. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97%.

(*trans*-3,3-Dibromo-2-phenylcyclopropyl)methyl 2-tetrahydropyranyl ether (20). Treatment of tetrahydropyranyl ether of (*E*)-cinnamyl alcohol (21.8 g, 100 mmol) with $CHBr_3$ (17.5 ml, 200 mmol) and *t*-BuOK (22.5 g, 200 mmol) as described for the synthesis of **13** gave the compound **20** in 57% yield (22.2 g, 57/43 diastereomeric mixture): Bp 110 °C (dec, 1 Torr, bath temp); IR (neat) 3056, 3028, 2938, 2866, 1654, 1602, 1498, 1465, 1452, 1387, 1364, 1351, 1323, 1261, 1201, 1183, 1120, 1077, 1063, 1034, 1001, 971, 950, 905, 869, 812, 753, 733, 694, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45–2.06 (m, 6H), 2.27 (ddd, *J*=7.5, 5.5, 3.2 Hz, 0.43H), 2.31 (ddd, *J*=7.7, 5.6, 3.5 Hz, 0.57H), 2.66 (d, *J*=7.7 Hz, 0.57H), 2.70 (d, *J*=7.5 Hz, 0.43H), 3.49–3.61 (m, 1H), 3.72–4.07 (m, 3H), 4.78 (bs, 1H), 7.25–7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.14, 19.35, 25.39, 30.52, 30.63, 34.35, 34.78, 39.62, 62.13, 62.27, 68.90, 69.13, 98.64, 98.97, 127.6, 128.3, 128.8, 135.6. Found: C, 46.30; H, 4.64%. Calcd for $C_{15}H_{18}O_2Br_2$: C, 46.18; H, 4.65%.

c*-2-Hydroxymethyl-*t*-3-phenyl-*r*-1-trimethylsilylcyclopropane (*cis*-21) and *t*-2-Hydroxymethyl-*c*-3-phenyl-*r*-1-trimethylsilylcyclopropane (*trans*-21).** Following the procedure for the synthesis of **14**, an addition of *n*-BuLi to a mixture of **20** (12.1 g, 31 mmol) and Me_3SiCl (19 ml, 150 mmol) in THF to give a silylated cyclopropane which was treated with *n*-Bu_3SnH-Et_3B followed by deprotection with *p*-TsOH gave **21** in 59% yield (4.0 g, ***cis*-21**/trans*-21** = 2/1).

Separation by PLC gave analytical samples (R_f=0.46 (***trans*-21**) and 0.51 (***cis*-21**), hexane/AcOEt = 3/1). ***cis*-21**: Bp 96 °C (1 Torr, bath temp); IR (neat) 3316, 3058, 3026, 2996, 2948, 2892, 1604, 1499, 1458, 1249, 1032, 920, 838, 751, 694, 662 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 9H), 0.25 (dd, *J*=10.0, 7.2 Hz, 1H), 1.46 (bs, 1H), 1.70 (dddd, *J*=10.0, 7.5, 7.0, 4.6 Hz, 1H), 1.82 (dd, *J*=7.2, 4.6 Hz, 1H), 3.63 (dd, *J*=11.2, 7.5 Hz, 1H), 3.70 (dd, *J*=11.2, 7.0 Hz, 1H), 7.08–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -0.14, 15.77, 26.51, 30.65, 64.91, 125.6, 125.8, 128.3, 143.4. Found: C, 71.13; H, 9.36%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%. ***trans*-21**: Bp 98 °C (1 Torr, bath temp); IR (neat) 3310, 3080, 3058, 3026, 2948, 2860, 1603, 1497, 1448, 1420, 1247, 1116, 1031, 905, 836, 791, 753, 697, 661 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.25 (s, 9H), 0.02 (dd, *J*=10.5, 7.0 Hz, 1H), 1.57 (bs, 1H), 1.70 (dtd, *J*=7.0, 6.6, 4.8 Hz, 1H), 2.25 (dd, *J*=10.5, 4.8 Hz, 1H), 3.66 (d, *J*=6.6 Hz, 2H), 7.10–7.27 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -1.10, 12.60, 23.51, 27.00, 68.21, 126.1, 127.9, 129.3, 140.0. Found: C, 70.58; H, 9.37%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

t*-2-Phenyl-*r*-1-trimethylsilyl-*c*-3-vinylcyclopropane (*cis*-22) and *c*-2-Phenyl-*r*-1-trimethylsilyl-*t*-3-vinylcyclopropane (*trans*-22).** Swern oxidation followed by Wittig reaction of **21** (3.13 g, 14.2 mmol) provided **22** in 82% yield (2.53 g, ***cis*-22**/trans*-22** = 2/1). ***cis*-22** (R_f=0.58, hexane): Bp 60 °C (1 Torr, bath temp); IR (neat) 3078, 3026, 2998, 2950, 1634, 1603, 1499, 1449, 1249, 1072, 984, 893, 839, 750, 694, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 9H), 0.47 (dd, *J*=9.7, 7.9 Hz, 1H), 1.92–2.04 (m, 2H), 4.97 (dd, *J*=9.9, 1.9 Hz, 1H), 5.16 (dd, *J*=16.8, 1.9 Hz, 1H), 5.48–5.68 (m, 1H), 7.06–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -0.37, 18.19, 29.12, 32.65, 113.9, 125.5, 125.7, 128.3, 139.6, 143.3. Found: C, 77.70; H, 9.47%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%. ***trans*-22** (R_f=0.65, hexane): Bp 55 °C (1 Torr, bath temp); IR (neat) 3078, 3058, 3024, 2996, 2950, 2894, 1636, 1603, 1497, 1448, 1248, 983, 959, 894, 856, 839, 752, 740, 697, 638

cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.25 (s, 9H), 0.23 (dd, *J*=10.5, 6.9 Hz, 1H), 1.98 (ddd, *J*=8.2, 6.9, 4.7 Hz, 1H), 2.37 (dd, *J*=10.5, 4.7 Hz, 1H), 4.92 (dd, *J*=10.0, 1.7 Hz, 1H), 5.19 (dd, *J*=17.1, 1.7 Hz, 1H), 5.57 (ddd, *J*=17.1, 10.0, 8.2 Hz, 1H), 7.10–7.27 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -1.01, 16.70, 24.87, 30.14, 111.7, 126.1, 127.9, 129.2, 140.2, 142.7. Found: C, 77.70; H, 9.52%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%.

1,2-Bis[(2-tetrahydropyranyloxy)methyl]-3,3-dibromocyclopropane (23). An addition of dibromocarbene ($CHBr_3$ (27.2 ml, 312 mmol) and *t*-BuOK (35 g, 312 mmol)) to tetrahydropyranyl ether of *cis*-2-buten-1,4-diol (20.3 g, 79.3 mmol) afforded the compound **23** (21.4 g) in 63% yield: Bp 158 °C (dec, 0.13 Torr, bath temp); IR (neat) 2938, 2868, 1466, 1453, 1440, 1386, 1366, 1353, 1263, 1201, 1183, 1135, 1121, 1077, 1060, 1032, 968, 905, 869, 815, 737 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54–1.93 (m, 12H), 2.03–2.17 (m, 2H), 3.44–3.63 (m, 4H), 3.75–4.00 (m, 4H), 4.65–4.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.06, 19.29, 25.35, 30.46, 30.54, 32.57, 32.77, 61.95, 62.00, 62.18, 65.25, 65.33, 98.62, 98.70, 98.83. Found: C, 42.05; H, 5.72%. Calcd for $C_{15}H_{24}O_4Br_2$: C, 42.08; H, 5.65%.

***c*-1,*c*-2-Bis[(2-tetrahydropyranyloxy)methyl]-*r*-3-bromo-3-trimethylsilylcyclopropane (*cis*-24) and *t*-1,*t*-2-Bis[(2-tetrahydropyranyloxy)methyl]-*r*-3-bromo-3-trimethylsilylcyclopropane (*trans*-24).** Treatment of **23** (16 g, 37 mmol) with *n*-BuLi (1.6 M, 25 ml, 40 mmol) in THF (100 ml) in the presence of Me_3SiCl (24 ml, 190 mmol) gave **24** in 64% yield (10.0 g, a mixture of two stereoisomers, 1/1). An isomer (R_f=0.55, hexane/AcOEt = 5/1): Bp 147 °C (dec, 0.13 Torr, bath temp); IR (neat) 2940, 2868, 1466, 1454, 1441, 1385, 1366, 1354, 1249, 1201, 1183, 1159, 1120, 1079, 1057, 1029, 976, 905, 868, 843, 815, 758, 630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.27 (s, 9H), 1.55–1.95 (m, 12H), 2.05–2.21 (m, 2H), 3.34–3.60 (m, 4H), 3.72–3.93 (m, 4H), 4.61–4.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.47, 19.12, 19.44, 25.38, 30.53, 30.65, 31.13, 32.46, 32.59, 61.82, 62.30, 63.42,

63.50, 63.88, 64.00, 98.33, 98.44. Found: C, 51.28; H, 8.09%. Calcd for $C_{18}H_{33}O_4SiBr$: C, 51.30; H, 7.89%. Another isomer (R_f=0.59, hexane/AcOEt = 5/1): Bp 140 °C (dec, 0,12 Torr, bath temp); IR (neat) 2940, 2868, 1466, 1454, 1441, 1385, 1366, 1354, 1283, 1250, 1201, 1184, 1161, 1137, 1120, 1078, 1057, 1029, 975, 905, 888, 868, 841, 816, 745, 620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 9H), 1.20–1.32 (m, 2H), 1.48–1.88 (m, 12H), 3.47–3.71 (m, 4H), 3.83–4.03 (m, 4H), 4.65–4.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -3.41, 19.27, 19.55, 21.78, 22.16, 25.43, 30.70, 34.63, 35.20, 62.00, 62.24, 62.30, 65.71, 65.85, 65.92, 98.40, 98.70. Found: C, 51.18; H, 8.16%. Calcd for $C_{18}H_{33}O_4SiBr$: C, 51.30; H, 7.89%.

c*-2,*c*-3-Bis[(2-tetrahydropyranyloxy)methyl]-*r*-1-trimethylsilylcyclopropane (*cis*-25) and *t*-2,*t*-3-Bis[(2-tetrahydropyranyloxy)methyl]-*r*-1-trimethylsilylcyclopropane (*trans*-25).** Reduction of **24** with *n*-Bu_3SnH-Et_3B afforded the compound **25** in 92% yield as a stereoisomeric mixture (cis*-25**/***trans*-25** = 17/1, GLPC Column A, 220 °C, t_r=3.57 min (***trans*-25**) and 4.63 min (***cis*-25**)): Bp 160 °C (1 Torr, bath temp); IR (neat) 2940, 2870, 1466, 1454, 1442, 1385, 1369, 1343, 1320, 1285, 1247, 1201, 1184, 1159, 1136, 1119, 1079, 1056, 1026, 973, 905, 886, 836, 815, 756, 686, 645 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.09–0.14 (m, 10H), 1.45–1.92 (m, 14H), 3.34–3.53 (m, 4H), 3.80–3.95 (m, 4H), 4.61–4.65 (m, 2H); ^{13}C NMR ($CDCl_3$) for ***cis*-25** δ 1.03, 7.67, 19.43, 19.61, 19.66, 20.06, 20.17, 25.49, 30.70, 30.82, 61.96, 62.04, 62.31, 62.36, 65.83, 65.93, 66.07, 98.53, 98.70. Found: C, 62.95; H, 10.25%. Calcd for $C_{18}H_{34}O_4Si$: C, 63.11; H, 10.00%.

***c*-3-Hydroxymethyl-*c*-2-(2-tetrahydropyranyloxy)methyl-*r*-1-trimethylsilylcyclopropane (*cis*-26).** Half deprotection of tetrahydropyranyl ether **25** (including two isomers) with *p*-TsOH in MeOH provided the title compound as a major product in 57% yield: Bp 134 °C (1 Torr, bath temp); IR (neat) 3432, 2944, 2892, 2872, 1442, 1413, 1383, 1285, 1248, 1202, 1160, 1133,

1119, 1078, 1053, 1025, 977, 903, 837, 758, 688, 646 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.07–0.08 (m, 10H), 1.10–1.90 (m, 8H), 2.91–3.65 (m, 4H), 3.79–3.93 (m, 2.5H), 4.11–4.19 (m, 0.5H), 4.68 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 1.31, 7.64, 7.73, 19.13, 19.47, 19.59, 19.77, 23.21, 23.29, 25.15, 25.26, 30.42, 30.54, 60.92, 61.11, 62.10, 62.45, 65.80, 66.20, 98.04, 98.80. Found: C, 60.13; H, 10.38%. Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14%.

***c*-2-Hydroxymethyl-*r*-1-trimethylsilyl-*c*-3-vinylcyclopropane (27).**

Starting from **26**, the compound **27** was obtained in 80% yield by the following sequence, Swern oxidation, Wittig reaction, and deprotection: Bp 81 °C (1 Torr, bath temp); IR (neat) 3326, 3076, 2996, 2952, 2892, 1633, 1411, 1286, 1249, 1024, 988, 945, 922, 897, 837, 757, 690, 665, 645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 9H), 0.17 (t, *J*=9.8 Hz, 1H), 1.44 (bs, 1H), 1.66 (dddd, *J*=9.8, 9.4, 8.0, 6.7 Hz, 1H), 1.96 (ddd, *J*=10.2, 9.8, 8.0 Hz, 1H), 3.65 (dd, *J*=11.3, 9.4 Hz, 1H), 3.82 (dd, *J*=11.3, 6.7 Hz, 1H), 5.05 (dd, *J*=10.2, 1.9 Hz, 1H), 5.27 (dd, *J*=16.8, 1.9 Hz, 1H), 5.69 (dt, *J*=16.8, 10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.97, 11.50, 24.42, 25.75, 61.59, 115.5, 136.4. Found: C, 63.17; H, 10.67%. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65%.

***c*-2-(1-Hydroxyethyl)-*r*-1-trimethylsilyl-*c*-3-vinylcyclopropane (28).**

Swern oxidation of **27** and successive treatment of the crude product with MeMgI gave **28** in 82% yield (threo/erythro = 1/1) by purification by silica-gel column chromatography. Diastereomers were seperated by PLC. Fast moving band (R_f=0.50, hexane/AcOEt = 3/1): Bp 75 °C (1 Torr, bath temp); IR (neat) 3314, 2966, 2952, 1633, 1367, 1286, 1261, 1247, 1186, 1108, 1099, 995, 982, 896, 833, 751, 689, 645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (t, *J*=9.5 Hz, 1H), 0.15 (s, 9H), 1.25 (d, *J*=6.1 Hz, 3H), 1.38 (ddd, *J*=10.3, 9.5, 8.3 Hz, 1H), 1.41 (bs, 1H), 1.92 (ddd, *J*=10.1, 9.5, 8.3 Hz, 1H), 3.58 (dq, *J*=10.3, 6.1 Hz, 1H), 5.00 (dd, *J*=10.1, 2.2 Hz, 1H), 5.20 (dd, *J*=16.8, 2.2 Hz, 1H), 5.57 (dt, *J*=16.8, 10.1 Hz, 1H); ^{13}C NMR

($CDCl_3$) δ 0.87, 12.10, 23.21, 24.82, 31.84, 67.31, 115.3, 136.6. Found: C, 65.10; H, 11.10%. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.93%. Slow moving band (R_f=0.44): Bp 76 °C (1 Torr, bath temp); IR (neat) 3368, 2952, 2896, 1634, 1283, 1251, 1105, 1063, 980, 967, 937, 895, 836, 757, 687, 645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 9H), 0.17 (t, *J*=9.6 Hz, 1H), 1.34 (d, *J*=6.1 Hz, 3H), 1.45 (ddd, *J*=10.3, 9.6, 7.9 Hz, 1H), 1.71 (bs, 1H), 1.90 (ddd, *J*=10.1, 9.6, 7.9 Hz, 1H), 3.70 (dq, *J*=10.3, 6.1 Hz, 1H), 5.08 (dd, *J*=10.1, 1.9 Hz, 1H), 5.29 (dd, *J*=16.9, 1.9 Hz, 1H), 5.73 (dt, *J*=16.9, 10.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.00, 12.35, 22.99, 24.38, 32.49, 67.03, 116.0, 136.5. Found: C, 65.15; H, 11.07%. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.93%.

***c*-2-Acetyl-*r*-1-trimethylsilyl-*c*-3-vinylcyclopropane (29).**

PCC (6.2 g, 28.9 mmol) oxidation of **28** (1.33 g, 7.2 mmol) provided the compound **29** in 65% yield (0.85 g, 4.7 mmol): Bp 58 °C (1 Torr, bath temp); IR (neat) 3080, 2996, 2948, 2896, 1699, 1634, 1425, 1388, 1351, 1284, 1246, 1172, 1136, 1031, 999, 977, 902, 872, 841, 765, 686, 643, 626, 604 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 9H), 0.49 (dd, *J*=10.1, 9.1 Hz, 1H), 2.24 (s, 3H), 2.32 (td, *J*=10.1, 8.3 Hz, 1H), 2.47 (dd, *J*=9.1, 8.3 Hz, 1H), 4.98 (dd, *J*=10.1, 2.2 Hz, 1H), 5.20 (dd, *J*=17.0, 2.2 Hz, 1H), 5.82 (dt, *J*=17.0, 10.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.79, 17.87, 31.81, 32.63, 115.2, 135.3, 207.3. Found: C, 65.71; H, 10.25%. Calcd for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95%.

***cis*-2-Hydroxymethyl-1-tributylstannylcyclopropane (30).**

CH_2I_2 (2 ml, 24 mmol) was added dropwise over 30 min to a mixture of 3-tributylstannyl-2-propen-1-ol[18] (4.3 g, 12.4 mmol), Et_2Zn (2.4 ml, 24 mmol) and *i*-Pr_2O (25 ml). After stirring for 1.5 h, workup and purification by silica-gel column chromatography (hexane/AcOEt = 5/1) gave **30** in 39% yield (1.72 g): Bp 123 °C (1 Torr, bath temp); IR (neat) 3336, 3048, 2952, 2920, 2868, 2850, 1458, 1419, 1376, 1071, 1028, 851 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.02 (ddd, *J*=9.7, 8.8,

7.5 Hz, 1H), 0.21 (ddd, *J*=7.5, 4.6, 3.8 Hz, 1H), 0.68–1.05 (m, 16H), 1.16–1.70 (m, 14H), 3.25 (dd, *J*=10.9, 7.8 Hz, 1H), 3.57 (dd, *J*=10.9, 6.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.40, 7.24, 9.76, 13.68, 17.46, 27.36, 29.09, 68.57. Found: C, 53.26; H, 9.76%. Calcd for $C_{16}H_{34}OSn$: C, 53.21; H, 9.49%.

***cis*-1-Tributylstannyl-2-vinylcyclopropane (31).** By means of Swern oxidation and Wittig reaction, the title compound **31** was obtained in 91% yield from **30**: Bp 70 °C (1 Torr, bath temp); IR (neat) 3078, 3048, 2954, 2922, 2868, 2848, 1635, 1458, 1419, 1376, 1340, 1289, 1072, 1033, 984, 960, 925, 893, 878, 834 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (ddd, *J*=9.8, 9.3, 7.9 Hz, 1H), 0.44 (ddd, *J*=7.9, 4.1, 3.8 Hz, 1H), 0.67–0.99 (m, 15H), 1.07 (ddd, *J*=9.3, 7.9, 3.8 Hz, 1H), 1.22–1.57 (m, 12H), 1.71 (dddd, *J*=9.8, 8.8, 7.9, 4.1 Hz, 1H), 4.87 (dd, *J*=9.9, 2.0 Hz, 1H), 5.10 (dd, *J*=17.0, 2.0 Hz, 1H), 5.30 (ddd, *J*=17.0, 9.9, 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 3.63, 9.71, 10.60, 13.73, 18.61, 27.36, 29.08, 112.2, 143.9. Found: C, 56.98; H, 9.87%. Calcd for $C_{17}H_{34}Sn$: C, 57.17; H, 9.59%.

***c*-2-Hydroxymethyl-*t*-3-methyl-*r*-1-tributylstannylcyclopropane (32).** CH_3CHI_2 (2.0 ml, 21 mmol) was added to a solution of 3-tributylstannyl-2-propen-1-ol (3.7 g, 11 mmol) and Et_2Zn (2.1 ml, 21 mmol) in *i*-Pr_2O (25 ml). Extractive workup followed by silica-gel column chromatography gave the compound **32** in 28% yield (1.11 g): Bp 120 °C (1 Torr, bath temp); IR (neat) 3312, 2950, 2920, 2852, 1459, 1419, 1377, 1357, 1341, 1291, 1249, 1073, 1019, 982, 961, 912, 873, 864, 685, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.27 (dd, *J*=9.1, 6.9 Hz, 1H), 0.60–1.68 (m, 33H, including 1.15 (d, *J*=5.7 Hz, 3H)), 3.23–3.37 (m, 1H), 3.46–3.59 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 8.33, 9.83, 13.71. 16.17, 20.78, 26.56, 27.35, 29.13, 68.10. Found: C, 54.39; H, 9.91%. Calcd for $C_{17}H_{36}OSn$: C, 54.42; H, 9.67%.

***t*-3-Methyl-*r*-1-tributylstannyl-*c*-2-vinylcyclopropane (33).** Swern oxidation ($(COCl)_2$ (0.30 ml, 3.5 mmol), DMSO (0.49 ml, 7.0 mmol), and Et_3N (1.9 ml, 14 mmol)) followed by Wittig reaction (Ph_3PCH_3I (1.22 g, 3.0 mmol) and

t-BuOK (0.34 g, 3.0 mmol)) afforded **33** in 88% yield (0.76 g) from **32** (0.87 g, 2.3 mmol): Bp 75 °C (1 Torr, bath temp); IR (neat) 3078, 2952, 2920, 2866, 2852, 2332, 1634, 1458, 1419, 1375, 1070, 975, 891, 667 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.01 (dd, *J*=9.2, 7.2 Hz, 1H), 0.65–1.65 (m, 32H including 1.15 (d, *J*=5.7 Hz, 3H)), 4.83 (dd, *J*=9.6, 2.3 Hz, 1H), 5.06 (dd, *J*=16.9, 2.3 Hz, 1H), 5.31 (ddd, *J*=16.9, 9.6, 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.72, 13.50, 13.73, 19.26, 20.63, 27.31, 28.01, 29.09, 111.7, 143.7. Found: C, 58.40; H, 10.06%. Calcd for $C_{18}H_{36}Sn$: C, 58.24; H, 9.78%.

General Procedure for the Radical Induced Ring Opening Reaction of Vinylcyclopropane. Procedure A: PhSH (1.1 mmol) was added to a solution of vinylcyclopropane (1.0 mmol) in benzene (2 ml) under argon atmosphere and the mixture was heated at 60 °C for several hours under stirring. The reaction mixture was concentrated *in vacuo* and the residue was purified by silica-gel column chromatography. Procedure B: Et_3B (1.0 M hexane solution, 0.2 ml) was added to a solution of vinylcyclopropane (1.0 mmol) and Ph_3SnH or *n*-Bu_3SnH (1.1 mmol) in benzene (3.0 ml) under argon atmosphere at room temperature. After stirring for several hours, the reaction mixture was concentrated *in vacuo* and the residual oil was purified by silica-gel column chromatography. Procedure C: In the case of the reaction between vinylcyclopropane and *n*-$C_6F_{13}I$ (1.2 mmol), hexane (2 ml) was used as a solvent instead of benzene in the Procedure B.

(*E*)-5-Dimethylphenylsilyl-1-phenylthio-2-pentene ((*E*)-39a) and (*Z*)-5-Dimethylphenylsilyl-1-phenylthio-2-pentene ((*Z*)-39a): Procedure A; GLPC Column A, 180 °C (initial) 220 °C (final) 2 °C/min, t_r=17.09 min ((***E*)-39a**) and 15.34 min ((***Z*)-39a**). **(*E*)-39a**: Bp 118 °C (1 Torr, bath temp); IR (neat) 3064, 3016, 2950, 2912, 2846, 1584, 1480, 1438, 1427, 1248, 1223, 1113, 1091, 1025, 965, 835, 819, 774, 735, 699, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 6H), 0.72–0.81 (m, 2H), 1.94–2.06 (m, 2H), 3.49 (d, *J*=6.0 Hz, 2H), 5.45 (dt, *J*=15.1,

6.6 Hz, 1H), 5.60 (dt, *J*=15.1, 6.0 Hz, 1H), 7.13–7.39 (m, 8H), 7.48–7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -3.05, 15.18, 26.51, 36.33, 123.5, 126.0, 127.7, 128.7, 128.8, 129.6, 133.5, 136.4, 136.9, 139.1. Found: C, 73.29; H, 7.85%. Calcd for $C_{19}H_{24}SiS$: C, 73.01; H, 7.74%. **(*Z*)-39a**: Bp 123 °C (1 Torr, bath temp); IR (neat) 3064, 3012, 2952, 2918, 1584, 1481, 1459, 1439, 1427, 1248, 1224, 1113, 1090, 1025, 909, 835, 816, 775, 734, 699, 689, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 6H), 0.67–0.76 (m, 2H), 1.90–2.02 (m, 2H), 3.48 (d, *J*=7.0 Hz, 2H), 5.41 (dt, *J*=11.0, 7.6 Hz, 1H), 5.52 (dt, *J*=11.0, 7.0 Hz, 1H), 7.13–7.37 (m, 8H), 7.45–7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -3.04, 15.85, 21.41, 31.33, 123.1, 126.3, 127.8, 128.8, 128.9, 130.3, 133.5, 136.2, 139.0, 139.5. Found: C, 73.26; H, 7.86%. Calcd for $C_{19}H_{24}SiS$: C, 73.01; H, 7.74%.

(*E*)-5-Dimethylphenylsilyl-1-triphenylstannyl-2-pentene ((*E*)-39b) and (*Z*)-5-Dimethylphenylsilyl-1-triphenylstannyl-2-pentene ((*Z*)-39b): Procedure B; LC t_r=42 min ((***E*)-39b**) and 45 min ((***Z*)-39b**). **(*E*)-39b**: Bp 210 °C (0.13 Torr, bath temp); IR (neat) 3060, 3044, 3010, 2950, 2902, 1654, 1480, 1428, 1248, 1113, 1074, 1022, 997, 959, 835, 772, 726, 697, 669, 657 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.21 (s, 6H), 0.65–0.73 (m, 2H), 1.89–2.00 (m, 2H), 2.36 (d, *J*=7.8 Hz, 2H), 5.42 (dt, *J*=15.0, 6.3 Hz, 1H), 5.63 (dt, *J*=15.0, 7.8 Hz, 1H), 7.33–7.73 (m, 20H); ^{13}C NMR ($CDCl_3$) δ -3.04, 15.78, 15.87, 26.71, 125.3, 127.7, 128.4, 128.8, 128.9, 131.4, 133.5, 137.1, 138.7, 139.4. Found: C, 67.00; H, 6.18%. Calcd for $C_{31}H_{34}SiSn$: C, 67.28; H, 6.19%. **(*Z*)-39b**: Bp 205 °C (0.13 Torr, bath temp); IR (neat) 3060, 3044, 3006, 2950, 2918, 1655, 1637, 1480, 1428, 1248, 1113, 1074, 1022, 997, 835, 818, 776, 725, 697, 656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 6H), 0.56–0.65 (m, 2H), 1.83–1.96 (m, 2H), 2.33 (d, *J*=8.9 Hz, 2H), 5.19 (dt, *J*=10.5, 6.9 Hz, 1H), 5.62 (dt, *J*=10.5, 8.9 Hz, 1H), 7.33–7.73 (m, 20H); ^{13}C NMR ($CDCl_3$) δ -3.12, 12.20, 15.62, 21.25, 124.5, 127.7, 128.4, 128.7, 128.9, 130.1, 133.5, 137.0, 138.6, 139.3. Found: C, 67.34; H, 6.17%. Calcd for $C_{31}H_{34}SiSn$: C,

67.28; H, 6.19%.

(*E*)-5-Dimethylphenylsilyl-1-tributylstannyl-2-pentene ((*E*)-39c) and (*Z*)-5-Dimethylphenylsilyl-1-tributylstannyl-2-pentene ((*Z*)-39c): Procedure B; LC t_r=42 min ((***E*)-39c**) and 44 min ((***Z*)-39c**). **(*E*)-39c**: Bp 150 °C (0.15 Torr, bath temp); IR (neat) 3066, 3006, 2952, 2920, 2868, 2850, 1654, 1648, 1459, 1427, 1376, 1248, 1114, 1069, 957, 836, 771, 726, 697, 662 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 6H), 0.68–1.02 (m, 17H), 1.23–1.63 (m, 12H), 1.66 (d, *J*=8.2 Hz, 2H), 1.92–2.04 (m, 2H), 5.25 (dt, *J*=15.0, 6.3 Hz, 1H), 5.50 (dt, *J*=15.0, 8.2 Hz, 1H), 7.33–7.38 (m, 3H), 7.49–7.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -2.99, 9.13, 13.74, 13.98, 16.21, 26.82, 27.35, 29.15, 127.6, 127.7, 128.4, 128.7, 133.6, 139.6. Found: C, 60.60; H, 9.58%. Calcd for $C_{25}H_{46}SiSn$: C, 60.85; H, 9.40%. **(*Z*)-39c**: Bp 119 °C (0.13 Torr, bath temp); IR (neat) 3066, 3046, 3002, 2952, 2920, 2868, 2848, 1637, 1459, 1388, 1376, 1248, 1114, 1071, 998, 900, 836, 817, 775, 727, 697, 663 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 6H), 0.68–1.02 (m, 17H), 1.23–1.63 (m, 12H), 1.66 (d, *J*=9.1 Hz, 2H), 1.96–2.07 (m, 2H), 5.07 (dt, *J*=10.6, 6.8 Hz, 1H), 5.46 (dt, *J*=10.6, 9.1 Hz, 1H), 7.34–7.39 (m, 3H), 7.50–7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -2.99, 9.30, 10.30, 13.73, 16.05, 21.03, 27.37, 29.16, 127.1, 127.2, 127.7, 128.8, 133.6, 139.5. Found: C, 60.97; H, 9.62%. Calcd for $C_{25}H_{46}SiSn$: C, 60.85; H, 9.40%.

(*E*)-5-Dimethylphenylsilyl-5-iodo-1-tridecafluorohexyl-2-pentene ((*E*)-39d) and (*Z*)-5-Dimethylphenylsilyl-5-iodo-1-tridecafluorohexyl-2-pentene ((*Z*)-39d): Procedure C; GLPC Column A, 190 °C, t_r=6.24 min ((***E*)-39d**) and 4.90 min ((***Z*)-39d**). **(*E*)-39d**: Bp 105 °C (1 Torr, bath temp); IR (neat) 3068, 2998, 2956, 2922, 1654, 1428, 1362, 1334, 1240, 1205, 1145, 1115, 1071, 1028, 968, 836, 815, 779, 734, 698, 651 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.48 (s, 6H), 2.39 (ddd, *J*=15.6, 10.6, 7.2 Hz, 1H), 2.54 (ddd, *J*=15.6, 6.2, 4.1 Hz, 1H), 2.78 (td, *J*=18.6, 6.9 Hz, 2H), 3.24 (dd, *J*=10.6, 4.1 Hz, 1H), 5.40 (dt, *J*=15.2, 6.9 Hz, 1H),

5.68 (ddd, *J*=15.2, 7.2, 6.2 Hz, 1H), 7.37–7.42 (m, 3H), 7.53–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -4.39, -2.59, 19.68, 34.60 (t, *J*=22.5 Hz), 36.92, 118.6 (t, *J*=4.1 Hz), 128.0, 129.7, 134.1, 135.8, 138.4; ^{19}F NMR ($CDCl_3$) δ -81.34 (bs, 3F), -113.4– -113.8 (m, 2F), -122.4 (bs, 2F), -123.5 (bs, 4F), -126.4– -126.8 (m, 2F). Found: C, 35.23; H, 2.75%. Calcd for $C_{19}H_{18}F_{13}SiI$: C, 35.20; H, 2.80%. **(*Z*)-39d**: Bp 89 °C (1 Torr, bath temp); IR (neat) 2954, 2920, 2850, 1654, 1429, 1364, 1346, 1315, 1239, 1204, 1144, 1115, 1067, 837, 814, 782, 733, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.48 (s, 3H), 0.50 (s, 3H), 2.39 (ddd, *J*=15.7, 10.4, 7.9 Hz, 1H), 2.53 (ddd, *J*=15.7, 6.6, 4.1 Hz, 1H), 2.68 (td, *J*=19.0, 7.0 Hz, 2H), 3.22 (dd, *J*=10.4, 4.1 Hz, 1H), 5.52 (dt, *J*=10.5, 7.0 Hz, 1H), 5.80 (ddd, *J*=10.5, 7.9, 6.6 Hz, 1H), 7.35–7.43 (m, 3H), 7.53–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -4.57, -2.62, 19.25, 29.55 (t, *J*=22.3 Hz), 31.62, 117.1 (t, *J*=4.0 Hz), 128.0, 129.7, 133.9, 135.6, 136.8. Found: C, 35.14; H, 2.82%. Calcd for $C_{19}H_{18}F_{13}SiI$: C, 35.20; H, 2.80%.

(*E*)-5-Dimethylphenylsilyl-4-methyl-1-phenylthio-2-pentene ((*E*)-40a): Procedure A; GLPC Column B, 210 °C, t_r=8.82 min; Bp 143 °C (1 Torr, bath temp); IR (neat) 3064, 3004, 2952, 2918, 2896, 2864, 1584, 1480, 1450, 1438, 1427, 1248, 1219, 1112, 1090, 1025, 967, 832, 792, 735, 698, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.25 (s, 6H), 0.74 (dd, *J*=14.6, 7.1 Hz, 1H), 0.83 (dd, *J*=14.6, 7.1 Hz, 1H), 0.90 (d, *J*=6.7 Hz, 3H), 2.15–2.36 (m, 1H), 3.43 (d, *J*=5.6 Hz, 2H), 5.33 (dt, *J*=15.0, 5.6 Hz, 1H), 5.42 (dd, *J*=15.0, 6.0 Hz, 1H), 7.12–7.37 (m, 8H), 7.45–7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -2.13, -2.01, 24.12, 32.98, 36.42, 121.7, 126.0, 127.6, 128.6, 128.7, 129.9, 133.5, 136.2, 139.7, 142.3. Found: C, 73.44; H, 8.10%. Calcd for $C_{20}H_{26}SiS$: C, 73.56; H, 8.02%.

(*Z*)-5-Dimethylphenylsilyl-4-methyl-1-phenylthio-2-pentene ((*Z*)-40a): Procedure A; GLPC Column B, 210 °C, t_r=7.60 min; Bp 139 °C (1 Torr, bath temp); IR (neat) 3066, 3006, 2952, 2920, 2864, 1726, 1480, 1438, 1427, 1248, 1113, 827, 793, 734, 689, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 3H), 0.28 (s,

3H), 0.76 (dd, *J*=14.7, 7.3 Hz, 1H), 0.85 (d, *J*=6.4 Hz, 3H), 0.86 (dd, *J*=14.7, 8.2 Hz, 1H), 2.43–2.66 (m, 1H), 3.33 (dd, *J*=13.4, 6.3 Hz, 1H), 3.45 (dd, *J*=13.4, 7.1 Hz, 1H), 5.27 (ddd, *J*=10.6, 7.1, 6.3 Hz, 1H), 5.34 (dd, *J*=10.6, 7.4 Hz, 1H), 7.14–7.38 (m, 8H), 7.46–7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -2.18, -1.86, 24.61, 24.83, 28.17, 31.33, 121.0, 126.1, 127.7, 128.7, 128.8, 129.8, 133.6, 136.4, 139.5, 141.8. Found: C, 73.57; H, 8.16%. Calcd for $C_{20}H_{26}SiS$: C, 73.56; H, 8.02%.

(*E*)-5-Dimethylphenylsilyl-4-methyl-1-triphenylstannyl-2-pentene ((*E*)-40b): Procedure B; LC t_r=41 min; Bp 230 °C (0.17 Torr, bath temp); IR (neat) 3060, 3044, 3010, 2952, 2894, 1480, 1429, 1247, 1113, 1074, 1022, 997, 962, 833, 792, 726, 697, 657 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (s, 3H), 0.22 (s, 3H), 0.69 (dd, *J*=14.7, 7.3 Hz, 1H), 0.78 (dd, *J*=14.7, 7.1 Hz, 1H), 0.84 (d, *J*=6.7 Hz, 3H), 2.10–2.31 (m, 1H), 2.31 (d, *J*=7.9 Hz, 2H), 5.27 (dd, *J*=15.1, 7.6 Hz, 1H), 5.54 (dt, *J*=15.1, 8.5 Hz, 1H), 7.31–7.50 (m, 20H); ^{13}C NMR ($CDCl_3$) δ -2.15, -2.01, 15.73, 24.37, 24.51, 33.17, 123.4, 127.6, 128.4, 128.6, 128.9, 133.5, 137.1, 137.2, 138.7, 140.1. Found: C, 67.93; H, 6.44%. Calcd for $C_{32}H_{36}SiSn$: C, 67.74; H, 6.39%.

(*E*),(*Z*)-5-Dimethylphenylsilyl-4-methyl-1-triphenylstannyl-2-pentene ((*E*)-40b:(*Z*)-40b = 73:27): Procedure B; LC t_r=43 min for **(*Z*)-40b**; Bp 190 °C (0.07 Torr, bath temp); IR (neat) 3060, 3044, 3010, 2952, 2918, 2896, 1481, 1459, 1450, 1428, 1300, 1247, 1189, 1113, 1075, 1022, 997, 963, 833, 795, 725, 696, 656 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (s, 3H), 0.22 (s,3H), 0.63 (d, *J*=6.6 Hz, 0.81H), 0.70–0.76 (m, 2H), 0.84 (d, *J*=6.7 Hz, 2.19H), 2.11–2.35 (m, 2.73H), 2.45–2.61 (m, 0.27H), 5.03 (dd, *J*=10.5, 9.6 Hz, 0.27H), 5.27 (dd, *J*=15.1, 7.6 Hz, 0.73H), 5.38–5.63 (m, 1H including 5.54 (dt, *J*=15.1, 8.5 Hz)), 7.30–7.69 (m, 20H). Found: C, 67.62; H, 6.47%. Calcd for $C_{32}H_{36}SiSn$: C, 67.74; H, 6.39%.

(*E*),(*Z*)-4-Methyl-1-phenylthio-5-trimethylsilyl-2-pentene ((*E*)-41:(*Z*)-41 = 88:12): Procedure A; Bp 115 °C (1 Torr, bath temp); IR (neat) 2950, 2920,

2892, 1585, 1480, 1452, 1439, 1415, 1294, 1248, 1219, 1120, 1090, 1068, 1025, 967, 855, 837, 783, 757, 736, 689, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 7.92H), 0.02 (s, 1.08H), 0.47–0.67 (m, 2H), 0.93 (d, *J*=7.0 Hz, 0.36H), 0.97 (d, *J*=6.7 Hz, 2.64H), 2.19–2.39 (m, 0.88H), 2.54–2.66 (m, 0.12H), 3.52 (d, *J*=5.8 Hz, 1.76H), 3.55 (dd, *J*=13.0, 6.2 Hz, 0.12H), 3.66 (dd, *J*=13.0, 6.6 Hz, 0.12H), 5.34–5.55 (m, 2H), 7.15–7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) for **(*E*)-41** δ - 0.65, 24.04, 25.05, 33.09, 36.53, 121.4, 126.0, 128.6, 129.9, 136.3, 142.7. Found: C, 67.92; H, 9.10%. Calcd for $C_{15}H_{24}SSi$: C, 68.11; H, 9.15%.

(*E*)-4,4-Dimethyl-1-phenylthio-5-trimethylsilyl-2-pentene (42a): Procedure A; GLPC Column B, 170 °C, t_R=6.29 min; Bp 105 °C (1 Torr, bath temp); IR (neat) 3056, 2950, 2876, 1584, 1480, 1458, 1438, 1418, 1379, 1361, 1247, 1092, 1025, 969, 856, 838, 761, 736, 688, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.02 (s,9H), 0.69 (s, 2H), 0.99 (s, 6H), 3.52 (d, *J*=6.8 Hz, 2H), 5.35 (dt, *J*=15.4, 6.8 Hz, 1H), 5.56 (d, *J*=15.4 Hz, 1H), 7.14–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 0.80, 30.37, 32.66, 35.77, 36.96, 119.1, 126.1, 128.7, 130.1, 136.3, 146.4. Found: C, 68.74; H, 9.66%. Calcd for $C_{16}H_{26}SiS$: C, 69.00; H, 9.41%.

(*E*)-5-Methyl-1-phenylthio-4-trimethylsilyl-2-hexene (43a): Procedure B; GLPC Column B, 170 °C, t_R=6.76 min; Bp 100 °C (1 Torr, bath temp); IR (neat) 3056, 3014, 2952, 2890, 1585, 1480, 1465, 1438, 1419, 1383, 1364, 1248, 1220, 1149, 1091, 1072, 1025, 970, 859, 837, 761, 736, 688, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ - 0.08 (s, 9H), 0.82 (d, *J*=6.8 Hz, 6H), 1.36 (dd, *J*=10.3, 4.9 Hz, 1H), 1.75–1.92 (m, 1H), 3.58 (d, *J*=6.7 Hz, 2H), 5.31 (dt, *J*=15.0, 6.7 Hz, 1H), 5.48 (dd, *J*=15.0, 10.3 Hz, 1H), 7.11–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ - 1.81, 20.63, 23.72, 28.34, 36.69, 41.25, 124.1, 125.8, 128.7, 129.5, 133.1, 140.2. Found: C, 69.01; H, 9.37%. Calcd for $C_{16}H_{26}SiS$: C, 69.00; H, 9.41%.

(*E*)-4,4-Dimethyl-5-trimethylsilyl-1-triphenylstannyl-2-pentene (42b): Procedure B; R_f=0.47 (hexane/AcOEt = 20/1); Bp 160 °C (0.10 Torr, bath temp);

IR (neat) 3060, 3046, 3010, 2950, 1481, 1466, 1460, 1429, 1247, 1075, 1022, 997, 966, 858, 840, 761, 725, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.05 (s, 9H), 0.63 (s, 2H), 0.93 (s, 6H), 2.37 (d, *J*=7.0 Hz, 2H), 5.42 (d, *J*=15.4 Hz, 1H), 5.53 (dt, *J*=15.4, 7.0 Hz, 1H), 7.33–7.48 (m, 9H), 7.52–7.73 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 0.77, 15.96, 30.59, 33.10, 35.68, 120.6, 128.4, 128.9, 137.1, 138.8, 141.1. Found: C, 64.83; H, 7.14%. Calcd for $C_{28}H_{36}SiSn$: C, 64.75; H, 6.99%.

(*E*)-5-Methyl-4-trimethylsilyl-1-triphenylstannyl-2-hexene (43b): Procedure B; R_f=0.42 (hexane/AcOEt = 20/1); Bp 165 °C (0.10 Torr, bath temp); IR (neat) 3060, 3044, 3008, 2950, 2894, 1481, 1460, 1428, 1300, 1258, 1247, 1075, 1023, 997, 962, 860, 837, 761, 726, 697, 657 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.14 (s, 9H), 0.75 (d, *J*=6.7 Hz, 6H), 1.26 (dd, *J*=10.3, 4.5 Hz, 1H), 1.69–1.85 (m, 1H), 2.45 (d, *J*=7.6 Hz, 2H), 5.31 (dd, *J*=15.2, 10.3 Hz, 1H), 5.50 (dt, *J*=15.2, 7.6 Hz, 1H), 7.33–7.48 (m, 9H), 7.52–7.73 (m, 6H); ^{13}C NMR ($CDCl_3$) δ -1.73, 16.27, 20.47, 23.70, 28.57, 41.13, 126.1, 127.0, 128.4, 128.9, 137.1, 138.7. Found: C, 64.52; H, 7.04%. Calcd for $C_{28}H_{36}SiSn$: C, 64.75; H, 6.99%.

(*E*)-5-Iodo-4,4-dimethyl-1-tridecafluorohexyl-5-trimethylsilyl-2-pentene (44): Procedure C; Bp 98 °C (1 Torr, bath temp); IR (neat) 2966, 1465, 1458, 1430, 1387, 1364, 1240, 1206, 1144, 1121, 1096, 1070, 1026, 974, 840, 808, 765, 746, 729, 698, 653 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.22 (s, 9H), 1.26 (s, 3H), 1.27 (s, 3H), 2.83 (td, *J*=18.3, 6.8 Hz, 2H), 3.33 (s, 1H), 5.37 (dt, *J*=15.6, 6.8 Hz, 1H), 5.80 (d, *J*=15.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.71, 28.17, 29.38, 34.80 (t, *J*=22.5 Hz), 40.49, 40.58, 113.7, 146.4. Found: C, 31.54; H, 3.29%. Calcd for $C_{16}H_{20}F_{13}SiI$: C, 31.28; H, 3.28%.

(*E*)-5-Methyl-1-tridecafluorohexyl-2,4-hexadiene (45): Procedure C; Bp 86 °C (20 Torr, bath temp); IR (neat) 3030, 2968, 2918, 2858, 1663, 1648, 1431, 1381, 1364, 1345, 1240, 1199, 1145, 1121, 1069, 1044, 986, 959, 894, 866, 845, 808, 778, 744, 728, 706, 697, 652 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77 (s, 3H), 1.79 (s,

3H), 2.88 (td, *J*=18.3, 7.6 Hz, 2H), 5.47 (dt, *J*=14.9, 7.6 Hz, 1H), 5.86 (d, *J*=11.0 Hz, 1H), 6.46 (dd, *J*=14.9, 11.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.33, 25.97, 34.97 (t, *J*=22.4 Hz), 116.0, 124.0, 133.9, 136.9. Found: C, 37.88; H, 2.69%. Calcd for $C_{13}H_{11}F_{13}$: C, 37.70; H, 2.68%.

(*E*),(*Z*)-5-Phenyl-1-phenylthio-4-trimethylsilyl-2-pentene ((*E*)-46a:(*Z*)-46a = 93:7): Procedure A; R_f=0.42 (hexane/AcOEt = 20/1); Bp 155 °C (1Torr, bath temp); IR (neat) 3056, 3022, 2950, 2918, 2850, 1584, 1495, 1480, 1453, 1438, 1248, 1121, 1088, 1069, 1025, 966, 839, 737, 690, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.08 (s, 8.37H), 0.04 (s, 0.63H), 1.83 (ddd, *J*=10.8, 9.1, 4.0 Hz, 0.93H), 2.16 (ddd, *J*=11.0, 7.0, 3.5 Hz, 0.07H), 2.49 (dd, *J*=13.8, 11.0 Hz, 0.07H), 2.58 (dd, *J*=14.3, 10.8 Hz, 0.93H), 2.80 (dd, *J*=14.3, 4.0 Hz, 0.93H), 2.89 (dd, *J*=13.8, 3.5 Hz, 0.07H), 3.27–3.30 (m, 0.14H), 3.48 (d, *J*=6.8 Hz, 1.86H), 5.22 (dt, *J*=15.2, 6.8 Hz, 0.93H), 5.30–5.47 (m, 0.14H), 5.47 (dd, *J*=15.2, 9.1 Hz, 0.93H), 7.08–7.32 (m, 10H); ^{13}C NMR ($CDCl_3$) for **(*E*)-46a** δ -3.23, 34.78, 34.98, 36.42, 123.1, 125.6, 125.7, 128.0, 128.5, 128.7, 129.2, 135.0, 136.5, 142.2. Found: C, 73.36; H, 8.09%. Calcd for $C_{20}H_{26}SiS$: C, 73.56; H, 8.02%.

(*E*),(*Z*)-4-Phenyl-1-phenylthio-5-trimethylsilyl-2-pentene ((*E*)-47a:(*Z*)-47a = 66:34): Procedure A; R_f=0.47 (hexane/AcOEt = 20/1); Bp 149 °C (1 Torr, bath temp); IR (neat) 3056, 3022, 2948, 2898, 1584, 1491, 1480, 1453, 1438, 1413, 1247, 1090, 1026, 967, 860, 837, 738, 698, 689, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.16 (s, 5.94H), -0.12 (s, 3.06H), 0.86 (dd, *J*=14.6, 7.3 Hz, 0.34H), 0.97 (d, *J*=7.8 Hz, 1.32H), 1.06 (dd, *J*=14.6, 7.9 Hz, 0.34H), 3.37 (td, *J*=7.8, 7.3 Hz, 0.66H), 3.49 (d, *J*=6.7 Hz, 1.32H), 3.53–3.76 (m, 1.02H), 5.40 (dt, *J*=10.7, 7.5 Hz, 0.34H), 5.48 (dt, *J*=15.1, 6.7 Hz, 0.66H), 5.68 (dd, *J*=15.1, 7.3 Hz, 0.66H), 5.70 (dd, *J*=10.7, 9.0 Hz, 0.34H), 7.07–7.35 (m, 10H); ^{13}C NMR ($CDCl_3$) for **(*Z*)-47a** δ -1.02, 1.01, 23.92, 25.67, 31.47, 36.53, 39.55, 44.52, 122.4, 123.2, 126.0, 126.1, 127.1, 127.2, 127.3, 128.3, 128.5, 128.7, 128.8, 129.8, 130.1, 136.0, 139.7, 140.4, 146.0; for

(*E*)-47a δ -1.02, 23.92, 36.53, 44.52, 123.2, 126.0, 126.1, 127.1, 127.3, 128.3, 128.7, 130.1, 140.4, 146.0. Found: C, 73.65; H, 8.10%. Calcd for $C_{20}H_{26}SiS$: C, 73.56; H, 8.02%.

(*E*),(*Z*)-5-Phenyl-4-trimethylsilyl-1-triphenylstannyl-2-pentene and (*E*),(*Z*)-4-phenyl-5-trimethylsilyl-1-triphenylstannyl-2-pentene ((*E*)-46b:(*Z*)-46b:(*E*)-47b:(*Z*)-47b = 80.4:11.3:5.3:3.0): Procedure B; Bp 190 °C (0.11 Torr, bath temp); IR (neat) 3060, 3044, 3014, 2948, 2900, 2850, 1494, 1481, 1453, 1429, 1247, 1108, 1075, 1022, 997, 960, 859, 838, 748, 726, 697, 657 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.23 (s, 0.270H), -0.19 (s, 0.477H), -0.13 (s, 7.236H), -0.08 (s, 1.017H), 0.78 (dd, *J*=14.5, 6.8 Hz, 0.030H), 0.87 (dd, *J*=14.5, 7.3 Hz, 0.053H), 0.96 (dd, *J*=14.5, 8.2 Hz, 0.053H), 0.97 (dd, *J*=14.5, 8.6 Hz, 0.030H), 1.72 (ddd, *J*=10.9, 7.9, 3.8 Hz, 0.804H), 2.13–2.54 (m, 3.030H), 2.74 (dd, *J*=14.0, 3.8 Hz, 0.917H), 3.25–3.36 (m, 0.053H), 3.60–3.72 (m, 0.030H), 5.10 (t, *J*=10.8 Hz, 0.113H), 5.22–5.70 (m, 1.887H), 6.95–7.17 (m, 5H), 7.23–7.65 (m, 15H); ^{1}H NMR ($CDCl_3$) for **(*E*)-46b** δ -0.13 (s, 9H), 1.72 (ddd, *J*=10.9, 7.9, 3.8 Hz, 1H), 2.35 (d, *J*=6.9 Hz, 2H), 2.48 (dd, *J*=14.0, 10.9 Hz, 1H), 2.74 (dd, *J*=14.0, 3.8 Hz, 1H), 5.28 (dd, *J*=15.0, 7.9 Hz, 1H), 5.37 (dt, *J*=15.0, 6.9 Hz, 1H), 6.95–7.17 (m, 5H), 7.23–7.65 (m, 15H); ^{13}C NMR ($CDCl_3$) for **(*E*)-46b** δ -3.12, 16.03, 35.03, 35.52, 125.1, 125.3, 128.0, 128.4, 128.6, 128.8, 129.2, 137.1, 138.7, 142.6. Found: C, 67.45; H, 6.51%. Calcd for $C_{32}H_{36}SiSn$: C, 67.74; H, 6.39%.

(*E*)-7-Phenylthio-4-trimethylsilyl-5-hepten-2-one (48a): Procedure A; Bp 102 °C (1 Torr, bath temp); IR (neat) 3056, 3016, 2950, 1709, 1654, 1648, 1584, 1480, 1438, 1419, 1356, 1249, 1171, 1118, 1090, 1025, 967, 841, 739, 689, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.13 (s, 9H), 1.99 (ddd, *J*=9.5, 8.0, 5.0 Hz, 1H), 2.03 (s, 3H), 2.33 (dd, *J*=16.0, 5.0 Hz, 1H), 2.43 (dd, *J*=16.0, 9.5 Hz, 1H), 3.50 (d, *J*=6.5 Hz, 2H), 5.28 (dt, *J*=15.4, 6.5 Hz, 1H), 5.43 (dd, *J*=15.4, 8.0 Hz, 1H), 7.09–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -3.44, 28.47, 29.73, 36.38, 43.02, 123.1,

125.9, 128.8, 129.5, 133.9, 136.0, 208.7. Found: C, 65.90; H, 8.43%. Calcd for $C_{16}H_{24}OSiS$: C, 65.70; H, 8.27%.

(*E*)-4-Trimethylsilyl-7-triphenylstannyl-5-hepten-2-one (48b): Procedure B; Bp 195 °C (0.15 Torr, bath temp); IR (neat) 3060, 3044, 3008, 2950, 1710, 1481, 1429, 1356, 1248, 1075, 997, 961, 909, 864, 838, 727 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.18 (s, 9H), 1.93 (ddd, *J*=8.8, 8.4, 6.6 Hz, 1H), 1.94 (s, 3H), 2.27 (dd, *J*=16.2, 6.6 Hz, 1H), 2.37 (dd, *J*=16.2, 8.4 Hz, 1H), 2.39 (d, *J*=7.7 Hz, 2H), 5.26 (dd, *J*=15.1, 8.8 Hz, 1H), 5.51 (dd, *J*=15.1, 7.7 Hz, 1H), 7.33–7.78 (m, 15H); ^{13}C NMR ($CDCl_3$) δ -3.40, 16.14, 28.54, 29.59, 43.47, 125.3, 128.0, 128.4, 128.9, 137.0, 138.5, 209.3. Found: C, 62.90; H, 6.49%. Calcd for $C_{28}H_{34}OSiSn$: C, 63.05; H, 6.43%.

(*E*),(*Z*)-1-Phenylthio-5-tributylstannyl-2-pentene ((*E*)-49:(*Z*)-49 = 92:8): Procedure A; Bp 150 °C (1 Torr, bath temp); IR (neat) 3056, 3016, 2952, 2920, 2868, 2848, 1585, 1480, 1458, 1438, 1418, 1375, 1070, 1025, 962, 735, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.63–0.96 (m, 17H), 1.20–1.58 (m, 12H), 2.00–2.11 (m, 0.16H), 2.12–2.23 (m, 1.84H), 3.52 (d, *J*=6.0 Hz, 1.84H), 3.56 (d, *J*=7.1 Hz, 0.16H), 5.40–5.70 (m, 2H including 5.48 (dt, *J*=15.2, 6.5 Hz), 5.62 (dt, *J*=15.2, 6.0 Hz)), 7.13–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) for (*E*)-isomer δ 8.20, 8.84, 13.74, 27.39, 29.22, 29.54, 36.41, 123.3, 125.9, 128.7, 129.6, 136.4, 137.8. Found: C, 59.10; H, 8.55%. Calcd for $C_{23}H_{40}SSn$: C, 59.11; H, 8.63%.

(*E*),(*Z*)-4-Methyl-1-phenylthio-5-tributylstannyl-2-pentene ((*E*)-50:(*Z*)-50 = 92.5:7.5): Procedure A; Bp 158 °C (1 Torr, bath temp); IR (neat) 3056, 2952, 2920, 2868, 2850, 1585, 1479, 1458, 1438, 1419, 1375, 1341, 1292, 1220, 1113, 1089, 1070, 1025, 1001, 964, 873, 735, 688, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.62–0.98 (m, 20H), 1.20–1.58 (m, 12H), 2.26–2.48 (m, 1H), 3.49 (d, *J*=5.7 Hz, 1.85H), 3.51 (dd, *J*=13.0, 6.2 Hz, 0.075H), 3.62 (dd, *J*=13.0, 6.5 Hz, 0.075H), 5.31–5.37 (m, 0.15H), 5.39 (dt, *J*=15.1, 5.7 Hz, 0.925H), 5.48 (dt, *J*=15.1, 6.0 Hz,

0.925H), 7.13–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) for **(*E*)-50** δ 9.40, 13.74, 18.22, 24.40, 27.45, 29.23, 34.96, 36.60, 121.4, 126.0, 128.7, 130.0, 136.3, 142.9. Found: C, 59.68; H, 8.66%. Calcd for $C_{24}H_{42}SSn$: C, 59.88; H, 8.79%.

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CHAPTER 3

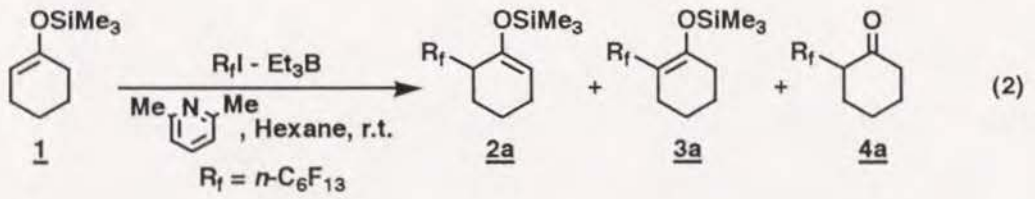
Triethylborane Induced Perfluoroalkylation of Silyl Enolates and Ketene Silyl Acetals with Perfluoroalkyl Iodides

Reaction of perfluoroalkyl iodides with silyl enolates mediated by Et_3B in the presence of base such as 2,6-dimethylpyridine provides mixtures of perfluoroalkylated trialkylsilyl enolates and α-perfluoroalkylated ketones. The yield and distribution of the products heavily depend on the nature of base employed. Treatment of a reaction mixture consisting of perfluoroalkylated silyl enolates and α-perfluoroalkylated ketone with concd HCl in THF gives α-perfluoroalkylated ketone as a single product. Reaction of ketene silyl acetals with perfluoroalkyl iodides in the absence of base affords α-perfluoroalkylated esters in excellent yields.

Recently, much attention has been paid to a method of introducing a perfluoroalkyl chain to a carbonyl compound and several reports have appeared in the literature.[1] The methods, however, have some drawbacks and there is still a need for a new method preparing perfluoroalkylated compounds from carbonyl compounds such as aldehydes, ketones, and esters. Previously we have reported that Et_3B induced the successful addition of perfluoroalkyl iodides (R_fI) to acetylenes and olefins (eq 1).[2] Here we report further exploitation of this method to (1) the reaction of R_fI with trialkylsilyl enolates providing perfluoroalkylated silyl enolates[3] and (2) the reaction of R_fI with ketene silyl acetals affording perfluoroalkylated esters.

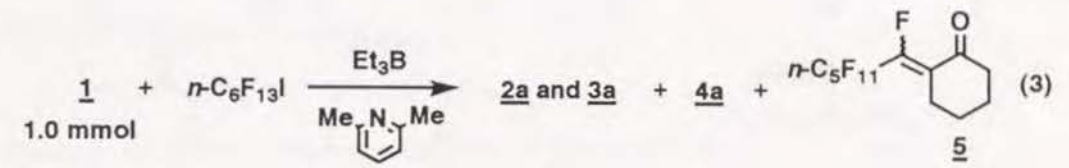
$$R_fI + CH_2{=}CHR \xrightarrow{Et_3B} \underset{R_f}{CH_2}\!-\!\underset{I}{CHR} \qquad (1)$$

(1) The reaction of perfluoroalkyl iodides with trialkylsilyl enolates. Treatment of a hexane solution of 1-trimethylsiloxy-1-cyclohexene (**1**) and *n*-$C_6F_{13}I$ with a catalytic amount of Et_3B[4] in the presence of base such as 2,6-dimethylpyridine gave a mixture of perfluoroalkylated silyl enolate **2a**, **3a** and 2-(perfluorohexyl)cyclohexanone (**4a**)[1d] in 76% combined yield (**2a**+**3a**/**4a** = 86/14, eq 2).



The distribution of the products heavily depends on the nature of base

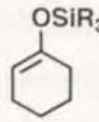
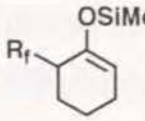
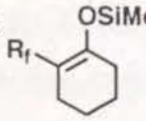
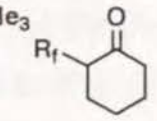
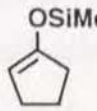
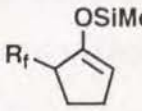
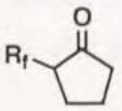
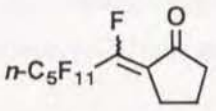
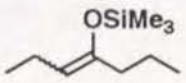
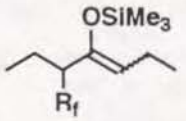
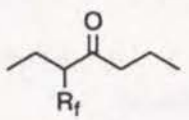
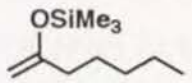
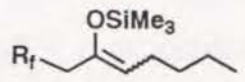
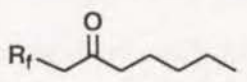
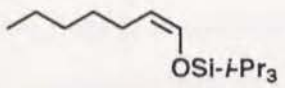
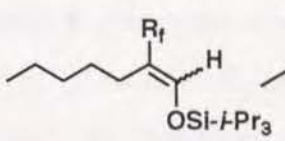
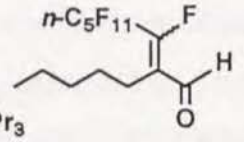
employed. The base and the yields of **2a**+**3a** (ratio of **2a**/**3a**) and **4a** in the reaction between 1-trimethylsiloxy-1-cyclohexene (**1**) and *n*-$C_6F_{13}I$ are given below: Et_3N, 47 (59/41), 26; 2,2,6,6-tetramethylpiperidine, 63 (68/32), 11; $(Me_3Si)_2NH$, 24 (0/100), 44; pyridine, 0, 20; *i*-Pr_2NEt, 12 (65/35), 29. The amount of base also affected the distribution of the products (eq 3). The presence of excess base (2,6-dimethylpyridine, 3.0 mmol per 1.0 mmol of silyl enolate) caused the formation of 2-(perfluorohexylidene)cyclohexanone (**5**) in 6% yield along with **2a**+**3a** (49%) and **4a** (23%). The use of slightly deficient amount of 2,6-dimethylpyridine suppressed the formation of **5**. The representative results using 2,6-dimethylpyridine (0.95 mmol per 1.0 mmol of silyl enolate) as a base are summarized in Table 1.



3.0 mmol	49%	23%	6%
1.0 mmol	59%	19%	0%
0.95 mmol	65%	11%	0%

The use of triisopropylsilyl enolate **6** instead of trimethylsilyl enolate **1** gave better yields of perfluoroalkylated silyl enolates **7** and **8** with less contamination by 2-(perfluoroalkyl)cyclohexanones **4** (Entries 3 and 4). Treatment of 1-trimethylsiloxy-1-cyclopentene (**9**) with *n*-$C_6F_{13}I$ gave a mixture of 5-(perfluorohexyl)-1-trimethylsiloxy-1-cyclopentene (**10**), 2-(perfluorohexyl)cyclopentanone (**11**), and 2-(perfluorohexylidene)cyclopentanone (**12**) in 35%, 26%, and 3% yield, respectively. 2-(Perfluorohexyl)-1-trimethylsiloxy-1-cyclopentene was not detected in the reaction mixture. The reaction proceeded with acyclic silyl enolate as well as cyclic silyl enolate. In the case of silyl enolate **13** or **16**, derived from acyclic ketone such as 4-heptanone or 2-heptanone, 5-(perfluoroalkyl)-4-trimethylsiloxy-3-heptenes **14**

Table 1. Reaction of Silyl Enolate with Perfluoroalkyl Iodide[a)]

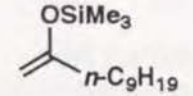
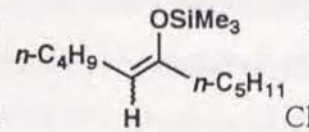
Entry	Silyl Enolate	R_fI	Product: Yield / % (E / Z)		
					
1	**1** (R = Me)	n-$C_6F_{13}I$	**2a**: 44	**3a**: 21	**4a**: 11
2	**1**	i-C_3F_7I	**2b**: 41	**3b**: 11	**4b**: 9
3	**6** (R = i-Pr)	n-$C_6F_{13}I$	**7a**: 57	**8a**: 14	**4a**: <5
4	**6**	i-C_3F_7I	**7b**: 47	**8b**: 25	**4b**: <2
					
5	**9**	n-$C_6F_{13}I$	**10**: 35	**11**: 26	**12**: 3
					
6	**13**	n-$C_6F_{13}I$	**14a**: 71 (60/40)	**15a**: 16	
7	**13**	i-C_3F_7I	**14b**: 66 (70/30)	**15b**: <2	
					
8	**16**	n-$C_6F_{13}I$	**17a**: 54 (28/72)	**18a**: 24	
9	**16**	i-C_3F_7I	**17b**: 56 (33/67)	**18b**: 15	
					
10	**19**	n-$C_6F_{13}I$	**20**: 38 (88/12 or 12/88)	**21**: 46 (71/29 or 29/71)	

a) Silyl enolate (2.0 mmol), R_fI (2.6 mmol), 2,6-dimethylpyridine (1.9 mmol), and Et_3B (0.40 mmol) were employed.

or 1-(perfluoroalkyl)-2-trimethylsiloxy-2-heptenes **17** was obtained as a single regioisomer as the reaction of 1-trimethylsiloxy-1-cyclopentene (**9**). The other isomeric silyl enolate 3-(perfluoroalkyl)-4-trimethylsiloxy-3-heptene or 1-(perfluoroalkyl)-2-trimethylsiloxy-1-heptene) was not observed in the reaction mixture. Reaction of silyl enolate **19** derived from heptanal afforded a mixture of 2-(perfluorohexyl)-1-triisopropylsiloxy-1-heptene (**20**) and 2-(perfluorohexylidene)-heptanal (**21**).

Treatment of the reaction mixture consisting of **2a**, **3a**, and **4a** with concd HCl in THF at room temperature for 10 min afforded 2-(perfluoroalkyl)cyclohexanone **4a** as a single product in 74% overall yield. The yields of perfluoroalkylated carbonyl compounds after acidic workup were 78%, 73%, and 56% for the reaction described in Entries 6, 8, and 9.

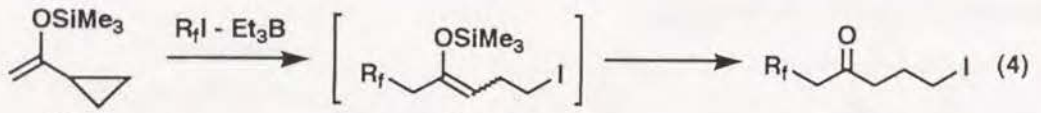
Table 2. Reaction of Silyl Enolate with CF_3I or CF_3CH_2I

Entry	Silyl Enolate (1.0 mmol)	RI (mmol)	Reaction Time / h	Product	Yield / %
1	 **22**	CF_3I (10)	40	CF_3CH_2CO-n-C_9H_{19} **23a**	64
2		CF_3CH_2I (2)	15	$CF_3(CH_2)_2CO$-n-C_9H_{19} **23b**	79
3	 **24**	CF_3I (10)	48	n-$C_4H_9CH(CF_3)CO$-n-C_5H_{11} **25a**	32
4		CF_3CH_2I (2)	20	n-$C_4H_9CH(CH_2CF_3)CO$-n-C_5H_{11} **25b**	4

Trifluoromethylated organic compounds are of importance from the biological point of view.[5)] Thus, we focussed our attention on trifluoromethylation of carbonyl compounds and examined the reactions of silyl enolate with CF_3I or

CF_3CH_2I (Table 2). Treatment of terminal silyl enolate **22** with excess CF_3I or CF_3CH_2I gave 1,1,1-trifluoro-3-dodecanone (**23a**) or 1,1,1-trifluoro-4-tridecanone (**23b**) in 64% or 79% yield, respectively after quenching the reaction mixture by concd HCl. Meanwhile, the reaction of internal silyl enolate such as **24** with CF_3I or CF_3CH_2I gave the corresponding trifluoro ketone **25a** or **25b** in poor yield.

Reaction of **26** prepared from cyclopropyl methyl ketone with R_fI followed by treatment with concd HCl provided the corresponding 5-iodo-1-(perfluoroalkyl)-2-pentanones under cleavage of cyclopropane ring.[6] The reaction proceeded without base such as 2,6-dimethylpyridine. The intermediary silyl enolate **27b** was isolated in the reaction of **26** with *i*-C_3F_7I in 85% yield (eq 4).

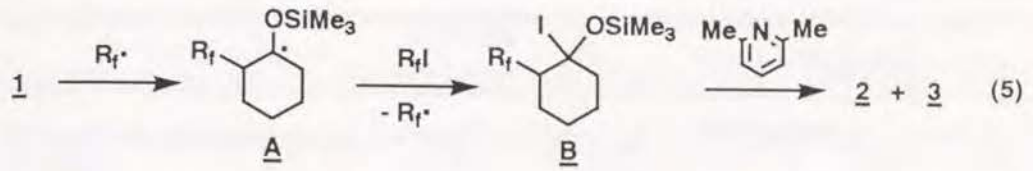


26 **27a-c** **28a-c**

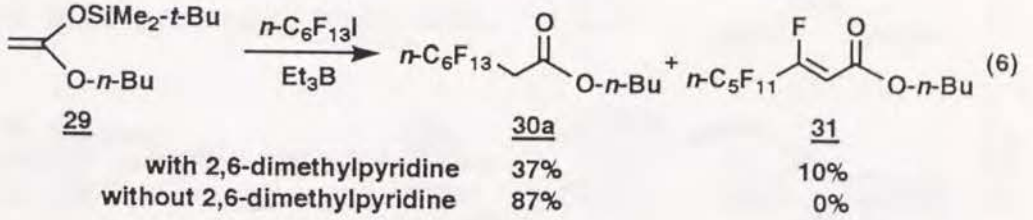
a: R_f = *n*-C_6F_{13}	r.t., 20 min	88%
b: R_f = *i*-C_3F_7	r.t., 20 min	83%
c: R_f = CF_3	-78 °C—5 °C, 3 h	67%

Thus, a new method provided us with a synthetic tool for the preparation of a newly functionalized trimethylsilyl enolate as well as α-perfluoroalkyl ketones.[7]

We are tempted to assume following reaction mechanism for the formation of perfluoroalkylated silyl enolates (eq 5): (1) Perfluoroalkyl radical, generated by the action of ethyl radical on R_fI, adds to silyl enolate to give a radical **A**, (2) the radical **A** abstracts iodine from R_fI to give the adduct **B** and regenerates perfluoroalkyl radical (R_f•), and (3) the coexisting base causes the elimination of HI to give a mixture of two perfluoroalkylated silyl enolate (**2** and **3**). The regioselective formation of **B** would be attributed to the electrophilic attack of reactive R_f• radical on the electron-rich carbon of silyl enolate.



(2) The reaction of perfluoroalkyl iodides with ketene silyl acetals. Reaction of ketene silyl acetals with R_fI also proceeded easily in the presence of Et_3B catalyst to give α-perfluoroalkylated esters in excellent yields. Exposure of ketene silyl acetal **29** (1.0 mmol) to *n*-$C_6F_{13}I$ (1.3 mmol) in the presence of 2,6-dimethylpyridine (0.95 mmol) provided butyl 2-(perfluorohexyl)acetate (**30a**, 37%) along with butyl 2-(perfluorohexylidene)acetate (**31**, 10%). In contrast, treatment of **29** (2.0 mmol) with *n*-$C_6F_{13}I$ (1.0 mmol) in the absence of 2,6-dimethylpyridine in hexane provided **30a** (87% based on *n*-$C_6F_{13}I$) as a single product (eq 6).

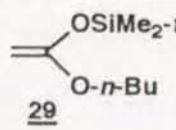
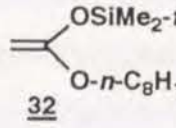
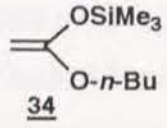
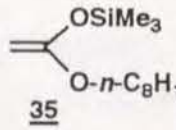
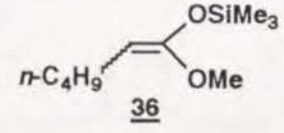
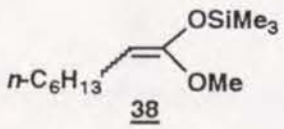
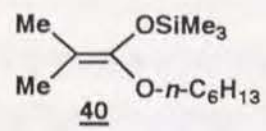


29 **30a** **31**

with 2,6-dimethylpyridine	37%	10%
without 2,6-dimethylpyridine	87%	0%

The yields of **30a** depend on the molar ratio of ketene silyl acetal and R_fI employed. The yields of **30a** in the reaction of **34** (x mmol) with *n*-$C_6F_{13}I$ (1.0 mmol) in the presence of catalytic amount of Et_3B (0.2 mmol) are as follows: **34** (2.0 mmol), 96%; **34** (1.5 mmol), 93%; **34** (1.2 mmol), 89%. Slight excess (1.2 equiv) of ketene silyl acetal was enough for the successful reaction. However, the reactions were performed using 2.0 equiv of ketene silyl acetals to obtain better yields and the results are summarized in Table 3.

Table 3. Reaction of Ketene Silyl Acetal with Perfluoroalkyl Iodide[a)]

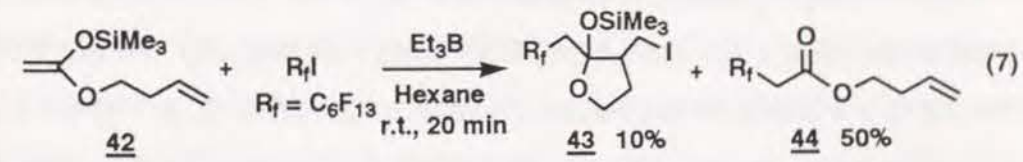
Entry	Ketene silyl acetal	R_fI	Reaction time / min	Product: Yield / %	
1	 **29**	n-$C_6F_{13}I$	10	R_fCH_2COO-n-Bu **30**	**30a**: 87
2		i-C_3F_7I	30		**30b**: 61
3	 **32**	CF_3I	120	R_fCH_2COO-n-C_8H_{17} **33**	**33b**: 81
4		CF_3CH_2I	30		**33c**: 62
5	 **34**	n-$C_6F_{13}I$	20[b)]	**30**	**30a**: 96
6		i-C_3F_7I	20		**30b**: 49
7	 **35**	i-C_3F_7I	20	**33**	**33a**: 96
8		CF_3I	120[b)]		**33b**: 90
9		CF_3CH_2I	60[b)]		**33c**: 77
10	 **36**	n-$C_6F_{13}I$	20	n-$C_4H_9CH(R_f)COOMe$ **37**	**37a**: 83
11		i-C_3F_7I	20		**37b**: 40
12	 **38**	i-C_3F_7I	20[b)]	n-$C_6H_{13}CH(R_f)COOMe$ **39**	**39a**: 88
13		CF_3I	120[b)]		**39b**: 66
14		CF_3CH_2I	120[b)]		**39c**: 32
15	 **40**	n-$C_6F_{13}I$	4 h	$R_fC(CH_3)_2COO$-n-C_6H_{13} **41**	**41a**: 63
16		i-C_3F_7I	16 h		**41b**: 27
17		CF_3I	12 h		**41c**: 22

a) Ketene silyl acetal (2.0 mmol), R_fI (1.0 mmol), and Et_3B (0.2 mmol) were employed.b) TBAF was added prior to work-up. See experimental part.

Not only n-$C_6F_{13}I$, i-C_3F_7I but also CF_3I[7)] or CF_3CH_2I reacted easily to give the corresponding perfluoroalkylated esters in good yields. Perfluoroalkylated ketene silyl acetal could not be detected. Trimethylsilyl acetal (**34** or **35**) reacted equally as t-butyldimethylsilyl acetal (**29** or **32**) to give the same perfluoroalkylated ester upon treatment with R_fI.

Alkyl group substituted ketene silyl acetals (**36**, **38**, and **40**) were prepared and their behavior toward R_fI were examined. Whereas the acetals **36** and **38** easily reacted with R_fI to provide the corresponding perfluoroalkylated esters in good yields, the acetal **40** reacted slowly because of its steric hindrance to give ester **41** in poor yields.

Treatment of ketene silyl acetal **42** with n-$C_6F_{13}I$ afforded a cyclized product **43** (10%) along with perfluoroalkylated ester **44** (50%) (eq 7). The formation of **43** suggests an intermediacy of carbon radical bearing OR and $OSiMe_3$ groups. The result also shows that C-C double bond of ketene silyl acetal is much more reactive than that of simple olefin.



(7)

Experimental

Preparation of Silyl Enolates. Trimethylsilyl enolates **1**, **9**, **13**, **16**, **22**, and **24** were prepared by the reported procedure.[8-11] Triisopropylsilyl enolate **6** and **19** were prepared according to the Corey's method.[12] 1-Trimethylsiloxy-1-cyclopropylethylene was obtained following the reported procedure.[13] The physical data are shown below for the silyl enolates whose physical data have not been described in the literature.

1-Triisopropylsiloxy-1-cyclohexene (6): Bp 91–96 °C (1 Torr, bath temp); IR (neat) 2936, 2892, 2864, 1670, 1465, 1367, 1195, 885, 826, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02–1.23 (m, 21H), 1.45–1.57 (m, 2H), 1.60–1.72 (m, 2H), 1.95–2.10 (m, 4H), 4.89 (t, *J*=3.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.66, 17.98, 22.38, 23.27, 23.87, 29.92, 103.6, 150.6; MS (70 eV) *m/z* (rel intensity) 254 (M^+, 11), 211 (100), 183 (26), 141 (18), 81 (20), 75 (48), 61 (36), 59 (28), 41 (20). Found: C, 70.54; H, 12.02%. Calcd for $C_{15}H_{30}OSi$: C, 70.80; H, 11.88%.

(Z)-1-Triisopropylsiloxy-1-heptene (19): Bp 81–86 °C (1 Torr, bath temp); IR (neat) 2926, 2864, 1655, 1465, 1256, 1135, 1092, 1069, 882, 683, 662 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.5 Hz, 3H), 1.03–1.20 (m, 21H), 1.22–1.42 (m, 6H), 2.04–2.15 (m, 2H), 4.39 (td, *J*=7.2, 5.8 Hz, 1H), 6.27 (dt, *J*=5.8, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.98, 14.10, 17.74, 22.57, 23.54, 29.39, 31.63, 110.0, 138.9; MS (70 eV) *m/z* (rel intensity) 270 (M^+, 2), 228 (20), 227 (100), 103 (21), 75 (24), 61 (15), 59 (29). Found: C, 70.94; H, 12.85%. Calcd for $C_{16}H_{34}OSi$: C, 71.04; H, 12.67%.

2-Trimethylsiloxy-1-undecene (22). This compound was prepared from 2-undecanone in 79% yield along with 2-trimethylsiloxy-2-undecene (93/7): Bp 85–86 °C (1 Torr); IR (neat) 2954, 2924, 2852, 1654, 1637, 1252, 1013, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9H), 0.88 (t, *J*=6.4 Hz, 3H), 1.20–1.53 (m, 14H), 2.01

(t, *J*=7.3 Hz, 2H), 4.04 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 0.15, 14.11, 22.70, 26.89, 29.15, 29.35, 29.52, 29.60, 31.93, 36.53, 89.75, 159.7; MS (70 eV) *m/z* (rel intensity) 242 (M^+, 4), 144 (14), 143 (100), 130 (70), 115 (40), 75 (52), 73 (97), 43 (18), 41 (21). Found: C, 69.57; H, 12.72%. Calcd for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47%.

(*E*) and (*Z*)-6-Trimethylsiloxy-5-undecene (24, (*E*):(*Z*) = 69:31). The title compound was prepared from 6-undecanone in 82% yield: Bp 75–78 °C (1 Torr); IR (neat) 2956, 2926, 2858, 1664, 1251, 1177, 1100, 888, 842 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 9H), 0.89 (t, *J*=6.5 Hz, 6H), 1.23–1.52 (m, 10H), 1.87–2.07 (m, 4H), 4.44 (t, *J*=6.8 Hz, 0.31H), 4.60 (t, *J*=7.6 Hz, 0.69H); ^{13}C NMR ($CDCl_3$) δ 0.37, 0.62, 14.03, 22.25, 22.58, 25.07, 26.57, 26.78, 31.13, 31.47, 31.56, 32.18, 32.96, 36.63, 107.8 (*E*), 108.4 (*Z*), 150.2 (*Z*), 151.4 (*E*); MS (70 ev) *m/z* (rel intensity) 243 (M^++1, 3), 242 (M^+, 14), 227 (9), 200 (18), 199 (100), 171 (9), 143 (14), 130 (23), 73 (15), 69 (10). Found: C, 69.09; H, 12.66%. Calcd for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47%.

The Reaction of Silyl Enolate with Perfluorohexyl or Perfluoroisopropyl Iodide in the Presence of Base (Procedure A). Perfluoroalkylation of cyclohexanone trimethylsilyl enolate is representative. Et_3B[4] (1.0 M hexane solution, 0.4 ml, 0.4 mmol) was added to a solution of 1-trimethylsiloxy-1-cyclohexene **1** (0.34 g, 2.0 mmol), *n*-$C_6F_{13}I$ (1.19 g, 2.6 mmol), and 2,6-dimethylpyridine (0.20 g, 1.9 mmol) in hexane (5 ml) at room temperature. After stirring for 8 h, resulting precipitate was filtered through Celite 545. The filtrate was concentrated *in vacuo*. The residual oil was submitted to silica-gel column chromatography to give perfluoroalkylated silyl enolate (**2a** and **3a**, 0.64 g, 65% yield, **2a/3a** = 68/32) and 2-(perfluorohexyl)cyclohexanone (**4a**,[14] 92 mg, 11% yield). Procedure A': Treatment of the reaction mixture consisting of **2a**, **3a**, and **4a** with acid afforded 2-(perfluoroalkyl)cyclohexanone (**4a**) as a single product. Thus,

the residual oil after concentration of the filtrate was treated with concd aqueous HCl (35 wt%, 1 ml) in THF (5 ml) for 10 min. Reaction mixture was slowly poured into saturated aqueous $NaHCO_3$ (40 ml) and extracted with AcOEt (30 ml x 2).[15] The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by silica-gel column chromatography gave only **4a** in 74% yield.

6-Perfluorohexyl-1-trimethylsiloxy-1-cyclohexene (2a): Bp 68–71 °C (1 Torr, bath temp); IR (neat) 2958, 1669, 1324, 1239, 1203, 1146, 1120, 913, 846, 694, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9H), 1.48–1.88 (m, 3H), 1.96–2.16 (m, 3H), 2.95 (tm, *J*=15.6 Hz, 1H), 5.11 (t, *J*=4.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -0.10, 18.82, 23.18 (two peaks), 41.77 (t, *J*=20.4 Hz), 108.6, 144.1, ^{13}C-Signals of perfluorohexyl group could not be observed for all perfluorohexyl compounds; ^{19}F NMR ($CDCl_3$) δ -81.39 (t, *J*=9.8 Hz, 3F), -108.1 (dm, *J*=284 Hz, 1F), -113.8 (dm, *J*=284 Hz, 1F), -121.2 (bs, 2F), -122.2 (bs, 2F), -123.2 (bs, 2F), -126.4– -126.8 (m, 2F); MS (70 eV) *m/z* (rel intensity) 488 (M^+, 10), 169 (14), 133 (12), 77 (61), 75 (6), 74 (8), 73 (100), 69 (27), 55 (19), 45 (11), 41 (17). Found: C, 37.17; H, 3.49%. Calcd for $C_{15}H_{17}F_{13}OSi$: C, 36.89; H, 3.51%.

2-Perfluorohexyl-1-trimethylsiloxy-1-cyclohexene (3a): Bp 68–72 °C (1 Torr, bath temp); IR (neat) 2944, 1661, 1375, 1292, 1238, 1204, 1145, 1119, 1074, 1065, 933, 861, 848, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9H), 1.55–1.75 (m, 4H), 2.14–2.19 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 0.50, 22.10, 22.45, 23.51 (t, *J*=5.0 Hz), 13 31.38, 117.1 (t, *J*=32.7 Hz), 155.8 (t, *J*=5.5 Hz); ^{19}F NMR ($CDCl_3$) δ -81.39 (tt, *J*=9.7, 3.6 Hz, 3F), -108.5 (t, *J*=14.0 Hz, 2F), -122.1– -123.2 (m, 6F), -126.4– -126.8 (m, 2F); MS (70 eV) *m/z* (rel intensity) 488 (M^+, 7), 220 (15), 219 (92), 169 (7), 77 (46), 74 (9), 73 (100), 69 (9), 45 (11), 41 (19). Found: C, 37.15; H, 3.56%. Calcd for $C_{15}H_{17}F_{13}OSi$: C, 36.89; H, 3.51%.

2-(Perfluorohexylidene)cyclohexanone (5): Bp 78–83 °C (7 Torr, bath

temp); IR (neat) 1722, 1228, 1204, 1164, 1144, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.81–2.05 (m, 4H), 2.54–2.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 25.01, 25.44, 27.45, 43.35, 129.2 (d, *J*=6.0 Hz), 198.5; ^{19}F NMR ($CDCl_3$) δ -81.28 (tt, *J*=9.8, 3.0 Hz, 3F), -114.1– -114.6 (m, 2F), -121.1 (bs, 1F), -123.3 (bs, 2F), -124.1 (bs, 2F), -126.4– -126.7 (m, 2F); MS (12 eV) *m/z* (rel intensity) 396 (M^+, 7), 369 (10), 368 (77), 150 (8), 149 (100), 127 (21), 99 (99), 67 (36), 41 (18). Found: C, 36.51; H, 2.09%. Calcd for $C_{12}H_8F_{12}O$: C, 36.38; H, 2.04%.

6-Perfluoroisopropyl-1-trimethylsiloxy-1-cyclohexene (2b): Bp 50–53 °C (1 Torr, bath temp); IR (neat) 2960, 1664, 1287, 1255, 1219, 1159, 1118, 1099, 985, 964, 936, 902, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 9H), 1.33–1.55 (m, 1H), 1.65–2.10 (m, 5H), 3.03–3.22 (m, 1H), 5.03 (t, *J*=4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -0.15, 20.92, 23.34, 23.56 (d, *J*=10.6 Hz), 41.08 (d, *J*=18.9 Hz), 93.92 (dm, *J*=205 Hz), 107.3, 121.2 (qd, *J*=289, 29.3 Hz), 145.2; ^{19}F NMR($CDCl_3$) δ -72.99 (d, *J*=4.9 Hz, 6F), -173.4– -173.9 (m, 1F); MS (70 eV) *m/z* (rel intensity) 338 (M^+, 19), 169 (27), 77 (64), 73 (100), 55 (11), 45 (14), 41 (14). Found: C, 42.76; H, 5.23%. Calcd for $C_{12}H_{17}F_7OSi$: C, 42.60; H, 5.06%.

2-Perfluoroisopropyl-1-trimethylsiloxy-1-cyclohexene (3b): Bp 50–55 °C (1 Torr, bath temp); IR (neat) 2942, 1669, 1369, 1299, 1272, 1259, 1217, 1172, 1144, 1065, 967, 956, 899, 848 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 9H), 1.55–1.76 (m, 4H), 2.10–2.21 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 0.89, 22.30 (d, *J*=3.7 Hz), 22.39, 23.67 (d, *J*=10.7 Hz), 31.35, 93.21 (dm, *J*=197 Hz), 101.5 (d, *J*=22.8 Hz), 121.3 (qd, *J*=288, 28.7 Hz), 153.1 (d, *J*=6.0 Hz); ^{19}F NMR ($CDCl_3$) δ -74.68 (d, *J*=6.1 Hz, 6F), -177.1 (sep, *J*=6.1 Hz, 1F); MS (70 eV) *m/z* (rel intensity) 338 (M^+, 17), 269 (11), 177 (10), 169 (27), 149 (13), 77 (50), 73 (100), 65 (10), 45 (16), 41 (24). Found: C, 42.49; H, 5.14%. Calcd for $C_{12}H_{17}F_7OSi$: C, 42.60; H, 5.06%.

2-(Perfluoroisopropyl)cyclohexanone (4b): Bp 82–87 °C (36 Torr, bath temp); IR (neat) 1733, 1292, 1274, 1224, 1161, 1134, 1109, 1098, 972 cm^{-1}; ^1H

NMR ($CDCl_3$) δ 1.60–2.15 (m, 5H), 2.30–2.60 (m, 3H), 3.16–3.30 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 24.61, 27.41, 28.45, 42.74, 51.95 (d, *J*=20.1 Hz), 92.61 (dm, *J*=207 Hz), 120.9 (qd, *J*=288, 27.4 Hz), 202.9 (d, *J*=4.8 Hz); ^{19}F NMR ($CDCl_3$) δ -72.85– -73.54 (m, 6F), -178.3– -178.9 (m, 1F); MS (70 eV) *m/z* (rel intensity) 266 (M^+, 71), 238 (11), 237 (16), 141 (15), 127 (13), 77 (10), 69 (18), 55 (100), 42 (20), 41 (14). Found: C, 40.90; H, 3.33%. Calcd for $C_9H_9F_7O$: C, 40.61; H, 3.41%.

6-Perfluorohexyl-1-triisopropylsiloxy-1-cyclohexene (7a): Bp 100–105 °C (1 Torr, bath temp); IR (neat) 2946, 2894, 2868, 1668, 1466, 1239, 1200, 1145, 1119, 883, 688, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01–1.26 (m, 21H), 1.55–1.83 (m, 2H), 2.00–2.18 (m, 4H), 2.85–3.10 (m, 1H), 5.08 (t, *J*=4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.75, 17.90 (d, *J*=3.9 Hz), 18.46, 23.08, 23.31, 41.54 (dd, *J*=21.0, 18.9 Hz), 107.2, 144.3 (t, *J*=2.7 Hz); ^{19}F NMR ($CDCl_3$) δ -81.29 (t, *J*=9.8 Hz, 3F), -107.6 (d, *J*=271 Hz, 1F), -113.5 (d, *J*=271 Hz, 1F), -121.4 (bs, 2F), -122.3 (bs, 2F), -123.2 (bs, 2F), -126.6 (bs, 2F); MS (70 eV) *m/z* (rel intensity) 572 (M^+, 2), 529 (30), 349 (17), 105 (50), 77 (100), 63 (13), 59 (13), 43 (34), 41 (17). Found: C, 44.22; H, 5.02%. Calcd for $C_{21}H_{29}F_{13}OSi$: C, 44.06; H, 5.11%.

2-Perfluorohexyl-1-triisopropylsiloxy-1-cyclohexene (8a): Bp 98–103 °C (1 Torr, bath temp); IR (neat) 2950, 2868, 1653, 1375, 1240, 1205, 1145, 1073 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03–1.30 (m, 21H), 1.58–1.80 (m, 4H), 2.10–2.32 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.69, 17.83, 22.14, 22.74, 23.82, 31.67, 102.5 (t, *J*=21.1 Hz), 156.3 (t, *J*=4.9 Hz); ^{19}F NMR ($CDCl_3$) δ -81.32 (t, *J*=9.8 Hz, 3F), -108.6 (bs, 2F), -122.4 (bs, 4F), -123.3 (bs, 2F), -126.4– -126.8 (m, 2F); MS (70 eV) *m/z* (rel intensity) 530 (M^+-^{i}Pr+1, 20), 529 (M^+-^{i}Pr, 79), 105 (50), 77 (100), 63 (15), 59 (12), 43 (24), 41 (19). Found: C, 43.81; H, 5.21%. Calcd for $C_{21}H_{29}F_{13}OSi$: C, 44.06; H, 5.11%.

6-Perfluoroisopropyl-1-triisopropylsiloxy-1-cyclohexene (7b): Bp 78–83

°C (1 Torr, bath temp); IR (neat) 2944, 2892, 2868, 1664, 1466, 1288, 1268, 1218, 1196, 1159, 1120, 1099, 1064, 965, 897, 882, 832, 677 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95–1.30 (m, 21H), 1.34–1.55 (m, 1H), 1.64–2.08 (m, 5H), 2.99–3.14 (m, 1H), 5.08 (t, *J*=4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.90, 17.90 (d, *J*=6.3 Hz), 20.85, 23.30, 23.72 (d, *J*=7.8 Hz), 40.94 (d, *J*=17.1 Hz), 93.86 (dm, *J*=208 Hz), 107.3, 121.2 (qd, *J*=288, 28.1 Hz), 146.0; ^{19}F NMR ($CDCl_3$) δ -72.73 (qd, *J*=8.6, 6.1 Hz, 3F), -73.65 (qd, *J*=8.6, 6.1 Hz, 3F), -172.1– -172.7 (m, 1F); MS (70 eV) *m/z* (rel intensity) 422 (M^+, 3), 379 (15), 199 (24), 179 (18), 159 (15), 105 (49), 79 (17), 77 (100), 63 (23), 59 (23), 43 (45), 41 (32). Found: C, 51.18; H, 6.99%. Calcd for $C_{18}H_{29}F_7OSi$: C, 51.17; H, 6.92%.

2-Perfluoroisopropyl-1-triisopropylsiloxy-1-cyclohexene (8b): Bp 76–81 °C (1 Torr, bath temp); IR (neat) 2946, 2896, 2870, 1645, 1467, 1371, 1293, 1216, 1180, 1160, 1146, 1067, 984, 968, 959, 898, 884, 844, 771 723 686 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99–1.26 (m, 21H), 1.52–1.74 (m, 4H), 2.07–2.26 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.83, 17.90, 22.38, 22.55, 24.03 (d, *J*=2.2 Hz), 32.26, 93.12 (dm, *J*=207 Hz), 99.00 (d, *J*=15.1 Hz), 121.5 (qd, *J*=289, 28.8 Hz), 155.2; ^{19}F NMR ($CDCl_3$) δ -74.74 (d, *J*=6.1 Hz, 6F), -177.2 (sep, *J*=6.1 Hz, 1F); MS (70 eV) *m/z* (rel intensity) 422 (M^+, 0.2), 379 (42), 227 (32), 207 (42), 179 (18), 105 (31), 77 (100), 63 (19), 43 (25), 41 (22). Found: C, 51.03; H, 6.98%. Calcd for $C_{18}H_{29}F_7OSi$: C, 51.17; H, 6.92%.

5-Perfluorohexyl-1-trimethylsiloxy-1-cyclopentene (10): Bp 65–70 °C (1 Torr, bath temp); IR (neat) 1666, 1654, 1381, 1240, 1205, 1146, 1120, 867, 848 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (s, 9H), 2.05–2.46 (m, 4H), 3.10–3.36 (m, 1H), 4.89 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ -0.43, 22.82, 27.07, 47.52 (dd, *J*=22.8, 20.3 Hz), 106.9, 148.9; ^{19}F NMR ($CDCl_3$) δ -81.33 (t, *J*=9.4 Hz, 3F), -109.5 (t, *J*=12.8 Hz, 1F), -116.0– -117.1 (m, 1F), -121.6 (bs, 1F), -122.1– -123.5 (m, 5F), -126.3– -126.8 (m, 2F); MS (70 eV) *m/z* (rel intensity) 475 (M^++1, 11), 474 (M^+,

52), 459 (25), 205 (39), 155 (15), 77 (54), 73 (100), 55 (59). Found: C, 35.50; H, 3.13%. Calcd for $C_{14}H_{15}F_{13}OSi$: C, 35.45; H, 3.19%.

2-(Perfluorohexyl)cyclopentanone (11): Bp 89–94 °C (5 Torr, bath temp); IR (neat) 2890, 2882, 1768, 1350, 1238, 1206, 1147, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.76–2.51 (m, 6H), 2.77–3.03 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 20.16, 24.51, 38.67, 49.29 (dd, *J*=24.1, 20.0 Hz), 208.9 (d, *J*=2.4 Hz); ^{19}F NMR ($CDCl_3$) δ -81.38 (tt, *J*=10.9, 2.4 Hz, 3F), -115.1– -116.0 (m, 2F), -121.3 (bs, 2F), -122.4 (bs, 2F), -123.2 (bs, 2F), -126.3– -126.8 (m, 2F); MS (70 eV) *m/z* (rel intensity) 403 (M^++1, 17), 402 (M^+, 100), 383 (11), 382 (46), 354 (12), 343 (8), 340 (10). Found: C, 32.77; H, 1.76%. Calcd for $C_{11}H_7F_{13}O$: C, 32.85; H, 1.75%.

2-(Perfluorohexylidene)cyclopentanone (12). Stereochemistry of alkene could not be determined: Bp 110–115 °C (37 Torr, bath temp); IR (neat) 1747, 1669, 1238, 1194, 1143, 1111, 724, cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.95–2.10 (m, 2H), 2.38–2.46 (m, 2H), 2.82–2.95 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.89, 25.83, 38.79, 141.9 (d, *J*=30.3 Hz), 202.6; ^{19}F NMR ($CDCl_3$) δ -81.34 (t, *J*=8.5 Hz, 3F), -116.6– -117.2 (m, 3F), -123.5 (bs, 4F), -126.6 (bs, 2F); MS (70 eV) *m/z* (rel intensity) 382 (M^+, 9), 135 (11), 121 (20), 113 (100), 107 (95), 69 (23), 57 (17), 55 (21). Found: C, 34.38; H, 1.51%. Calcd for $C_{11}H_6F_{12}O$: C, 34.57; H, 1.58%.

(*Z*)-5-Ethyl-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-4-trimethylsiloxy-3-undecene ((*Z*)-14a): Bp 95–100 °C (35 Torr, bath temp); IR (neat) 2966, 1671, 1362, 1299, 1240, 1195, 1147, 1121, 1087, 847, 733, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9H), 0.95 (t, *J*=7.4 Hz, 3H), 0.96 (t, *J*=7.5 Hz, 3H), 1.58–1.85 (m, 2H), 1.92–2.15 (m, 2H), 2.60 (tdd, *J*=14.8, 10.3, 4.3 Hz, 1H), 4.59 (t, *J*=7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.83, 11.55, 14.01, 18.07, 19.33, 50.47 (t, *J*=20.5 Hz), 115.5, 141.9; ^{19}F NMR ($CDCl_3$) δ -81.30 (tt, *J*=9.8, 2.4 Hz, 3F), -113.8– -114.7 (m, 2F), -121.2 (bs, 2F), -122.3 (bs, 2F), -123.3 (bs, 2F), -126.3– -126.7 (m, 2F); MS (70 eV) *m/z* (rel intensity) 504 (M^+, 23), 489 (10), 448 (9), 207 (14), 143 (14), 77

(34), 73 (100), 70 (14), 69 (9), 55 (30). Found: C, 37.82; H, 4.03%. Calcd for $C_{16}H_{21}F_{13}OSi$: C, 38.10; H, 4.20%.

(*E*)-5-Ethyl-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-4-trimethylsiloxy-3-undecene ((*E*)-14a): Bp 50–55 °C (1 Torr, bath temp); IR (neat) 2966, 1664, 1241, 1146, 962, 886, 848, 659 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 9H), 0.90 (t, *J*=7.4 Hz, 3H), 0.96 (t, *J*=7.4 Hz, 3H), 1.60–2.08 (m, 4H), 3.07 (tdd, *J*=15.1, 10.5, 4.1 Hz, 1H), 4.77 (t, *J*=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.00, 11.15, 14.83, 17.24, 20.16, 43.85 (t, *J*=20.7 Hz), 112.9, 143.0; ^{19}F NMR ($CDCl_3$) δ -81.35 (t, *J*=9.8 Hz, 3F), -113.6 (bs, 2F), -121.8– -122.4 (m, 4F), -123.2 (bs, 2F), -126.4– -126.9 (m, 2F); MS (70 eV) *m/z* (rel intensity) 505 (M^++1, 12), 504 (M^+, 53), 489 (22), 448 (20), 207 (24), 143 (17), 77 (36), 73 (100), 55 (27). Found: C, 38.33; H, 4.04%. Calcd for $C_{16}H_{21}F_{13}OSi$: C, 38.10; H, 4.20%.

5-Ethyl-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-4-undecanone (15a): Bp 97–102 °C (35 Torr, bath temp); IR (neat) 2970, 1731, 1363, 1239, 1207, 1146, 694, 651 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, *J*=7.3 Hz, 6H), 1.55–1.73 (m, 2H), 1.78–2.09 (m, 2H), 2.46 (dt, *J*=18.4, 7.2 Hz, 1H), 2.60 (dt, *J*=18.4, 7.3 Hz, 1H), 3.21 (tdd, *J*=15.0, 10.2, 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.39, 13.31, 16.37, 18.81 (t, *J*=5.1 Hz), 46.19, 54.85 (t, *J*=19.8 Hz), 204.1; ^{19}F NMR ($CDCl_3$) δ -81.32 (tt, *J*=9.8, 2.4 Hz, 3F), -113.6– -114.1 (m, 2F), -121.1 (bs, 2F), -122.3 (bs, 2F), -123.3 (bs, 2F), -126.3– -126.8 (m, 2F); MS (70 eV) *m/z* (rel intensity) 432 (M^+, 0.5), 388 (5), 72 (5), 71 (100), 69 (6), 47 (14), 43 (55), 41 (11). Found: C, 35.88; H, 2.98%. Calcd for $C_{13}H_{13}F_{13}O$: C, 36.13; H, 3.03%.

(*Z*)-5-Ethyl-6,7,7,7-tetrafluoro-6-trifluoromethyl-4-trimethylsiloxy-3-heptene ((*Z*)-14b): Bp 82–87 °C (35 Torr, bath temp); IR (neat) 2966, 1670, 1384, 1298, 1256, 1224, 1186, 1160, 1127, 1101, 1088, 1069, 952, 847 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9H), 0.95 (t, *J*=7.4 Hz, 6H), 1.58–1.85 (m, 2H), 1.97–2.12 (m, 2H), 2.56–2.70 (m, 1H), 4.63 (t, *J*=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.92,

12.50, 13.89, 18.56, 19.54, 50.43 (d, *J*=20.1 Hz), 92.76 (dm, *J*=204 Hz), 115.5, 121.1 (qd, *J*=288, 28.8 Hz), 121.3 (qd, *J*=289, 26.6 Hz), 141.5 (d, *J*=6.5 Hz); ^{19}F NMR ($CDCl_3$) δ -73.10 (d, *J*=7.3 Hz, 6F), -174.7– -175.7 (m, 1F); MS (70 eV) *m/z* (rel intensity) 355 (M^++1, 12), 354 (M^+, 62), 339 (47), 298 (49), 247 (14), 185 (22), 143 (16), 77 (31), 73 (100). Found: C, 44.14; H, 6.08%. Calcd for $C_{13}H_{21}F_7OSi$: C, 44.06; H, 5.97%.

(*E*)-5-Ethyl-6,7,7,7-tetrafluoro-6-trifluoromethyl-4-trimethylsiloxy-3-heptene ((*E*)-14b): Bp 77–82 °C (35 Torr, bath temp); IR (neat) 2966, 1661, 1297, 1255, 1224, 1159, 1135, 1123, 892, 848 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9H), 0.87 (t, *J*=7.3 Hz, 3H), 0.96 (t, *J*=7.5 Hz, 3H), 1.57–2.06 (m, 4H), 3.04–3.18 (m, 1H), 4.75 (t, *J*=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -0.26, 11.91, 14.82, 17.93, 20.31, 43.79 (d, *J*=20.5 Hz), 92.51 (dm, *J*=203 Hz), 113.3, 121.1 (qd, *J*=290, 27.3 Hz), 121.4 (qd, *J*=290, 27.6 Hz), 142.3 (d, *J*=6.0 Hz); ^{19}F NMR ($CDCl_3$) δ -72.98– -73.91 (m, 6F), -174.7– -176.1 (m, 1F); MS (70 eV) *m/z* (rel intensity) 354 (M^+, 11), 339 (9), 298 (12), 185 (9), 143 (9), 77 (33), 73 (100), 55 (10). Found: C, 44.18; H, 6.22%. Calcd for $C_{13}H_{21}F_7OSi$: C, 44.06; H, 5.97%.

5-Ethyl-6,7,7,7-tetrafluoro-6-trifluoromethyl-4-heptanone (15b): Bp 71–76 °C (49 Torr, bath temp); IR (neat) 2968, 2938, 1733, 1299, 1260, 1226, 1163, 1145, 1131, 971 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J*=7.9 Hz, 3H), 0.93 (t, *J*=7.4 Hz, 3H), 1.55–1.89 (m, 3H), 1.93–2.17 (m, 1H), 2.43 (dtd, *J*=18.3, 7.0, 1.2 Hz, 1H), 2.64 (dtd, *J*=18.3, 7.3, 1.6 Hz, 1H), 3.10–3.25 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 12.31, 13.25, 16.57, 19.00, 48.06, 53.00 (d, *J*=8.6 Hz), 92.19 (dm, *J*=205 Hz), 120.6 (qd, *J*=287, 27.7 Hz), 120.8 (qd, *J*=287, 28.0 Hz), 204.1; ^{19}F NMR ($CDCl_3$) δ -73.05 (dq, *J*=8.6, 8.5 Hz, 3F), -74.43 (dq, *J*=9.8, 8.5 Hz, 3F), -176.4– -176.9 (m, 1F); MS (70 eV) *m/z* (rel intensity) 239 (M^+-C_3H_7, 2), 171 (2), 127 (3), 72 (5), 71 (100), 43 (88), 41 (24). Found: C, 42.30; H, 4.46%. Calcd for $C_{10}H_{13}F_7O$: C, 42.56; H, 4.64%.

(*Z*)-8,8,9,9,10,10,11,11,12,12,13,13,13-Tridecafluoro-6-trimethylsiloxy-5-tridecene ((*Z*)-17a): Bp 94–99 °C (5 Torr, bath temp); IR (neat) 2958, 2930, 1675, 1350, 1240, 1195, 1145, 1121, 1097, 990, 846, 707 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9H), 0.90 (t, *J*=6.8 Hz, 3H), 1.25–1.37 (m, 4H), 1.99–2.10 (m, 2H), 2.75 (t, *J*=18.4 Hz, 2H), 4.72 (t, *J*=7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.37, 13.82, 22.41, 25.55, 31.61, 38.32 (t, *J*=22.1 Hz), 116.5, 139.1; ^{19}F NMR ($CDCl_3$) δ -81.32 (t, *J*=9.8 Hz, 3F), -113.0– -113.5 (m, 2F), -122.1– -122.6 (m, 2F), -123.4 (bs, 2F), -123.8 (bs, 2F), -126.3– -126.9 (m, 2F); MS (70 eV) *m/z* (rel intensity) 505 (M^++1, 7), 504 (M^+, 27), 462 (14), 461 (89), 175 (10), 77 (17), 73 (100), 55 (38). Found: C, 37.90; H, 4.15%. Calcd for $C_{16}H_{21}F_{13}OSi$: C, 38.10; H, 4.20%.

(*E*)-8,8,9,9,10,10,11,11,12,12,13,13,13-Tridecafluoro-6-trimethylsiloxy-5-tridecene ((*E*)-17a): Bp 71–76 °C (1 Torr, bath temp); IR (neat) 2960, 2930, 1670, 1360, 1240, 1195, 1145, 1122, 847, 733, 707 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9H), 0.90 (t, *J*=7.0 Hz, 3H), 1.27–1.37 (m, 4H), 1.89–2.00 (m, 2H), 2.86 (t, *J*=18.4 Hz, 2H), 4.91 (t, *J*=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.09, 13.87, 22.19, 26.91, 32.31, 33.26 (t, *J*=22.2 Hz), 113.5, 140.6; ^{19}F NMR ($CDCl_3$) δ -81.32 (t, *J*=9.8 Hz, 3F), -112.3– -112.7 (m, 2F), -122.3 (bs, 2F), -123.4 (bs, 2F), -123.8 (bs, 2F), -126.4– -126.9 (m, 2F); MS (70 eV) *m/z* (rel intensity) 504 (M^+, 6), 461 (23), 175 (8), 77 (22), 74 (9), 73 (100), 55 (46). Found: C, 38.25; H, 4.17%. Calcd for $C_{16}H_{21}F_{13}OSi$: C, 38.10; H, 4.20%.

8,8,9,9,10,10,11,11,12,12,13,13,13-Tridecafluoro-6-tridecanone (18a): Bp 100–105 °C (43 Torr, bath temp); IR (neat) 2960, 2934, 1732, 1363, 1240, 1204, 1145, 1124, 706 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J*=6.7 Hz, 3H), 1.23–1.40 (m, 4H), 1.55–1.70 (m, 2H), 2.58 (t, *J*=7.3 Hz, 2H), 3.16 (t, *J*=18.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.84, 22.37, 22.88, 31.03, 43.10 (t, *J*=22.1 Hz), 44.48, 200.0; ^{19}F NMR ($CDCl_3$) δ -81.29 (bs, 3F), -111.2– -112.0 (m, 2F), -122.2 (bs, 2F), -123.4 (bs, 4F), -126.3– -126.8 (m, 2F); MS (70 eV) *m/z* (rel intensity) 432 (M^+,

5), 376 (100), 361 (45), 356 (95), 341 (47), 99 (45), 56 (36), 43 (61). Found: C, 36.06; H, 2.94%. Calcd for $C_{13}H_{13}F_{13}O$: C, 36.13; H, 3.03%.

(*Z*)-1,1,1,2-Tetrafluoro-2-trifluoromethyl-4-trimethylsiloxy-4-nonene ((*Z*)-17b): Bp 50–55 °C (1 Torr, bath temp); IR (neat) 2958, 2930, 1675, 1378, 1332, 1286, 1221, 1187, 1163, 1151, 1117, 1069, 999, 978, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 9H), 0.89 (t, *J*=6.5 Hz, 3H), 1.26–1.36 (m, 4H), 1.94–2.06 (m, 2H), 2.73 (d, *J*=21.5 Hz, 2H), 4.71 (t, *J*=7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.46, 13.88, 22.29, 25.39, 31.39, 36.08 (d, *J*=19.7 Hz), 91.39 (dm, *J*=206 Hz), 116.3, 120.8 (qd, *J*=288, 27.9 Hz), 139.9 (d, *J*=2.8 Hz); ^{19}F NMR ($CDCl_3$) δ -76.60 (d, *J*=7.3 Hz, 6F), -183.0 (tsep, tsep = triplet, septet, *J*=22.0, 7.3 Hz, 1F); MS (70 eV) *m*/*z* (rel intensity) 354 (M^+, 4), 311 (22), 219 (10), 77 (15), 74 (9), 73 (100). Found: C, 43.95; H, 6.02%. Calcd for $C_{13}H_{21}F_7OSi$: C, 44.06; H, 5.97%.

(*E*)-1,1,1,2-Tetrafluoro-2-trifluoromethyl-4-trimethylsiloxy-4-nonene ((*E*)-17b): Bp 49–54 °C (1 Torr, bath temp); IR (neat) 2958, 2932, 1671, 1332, 1286, 1224, 1187, 1163, 1118, 998, 918, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 9H), 0.90 (t, *J*=7.0 Hz, 3H), 1.25–1.37 (m, 4H), 1.89–2.02 (m, 2H), 2.86 (d, *J*=20.8 Hz, 2H), 4.80 (t, *J*=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -0.08, 13.90, 22.25, 26.87, 30.89 (d, *J*=20.9 Hz), 32.28, 91.21 (dm, *J*=206 Hz), 112.5, 120.8 (qd, *J*=286, 24.5 Hz), 141.0; ^{19}F NMR ($CDCl_3$) δ -76.82 (d, *J*=6.1 Hz, 6F), -182.3 (tsep, *J*=20.8, 6.1 Hz, 1F); MS (70 eV) *m*/*z* (rel intensity) 354 (M^+, 22), 312 (18), 311 (100), 298 (15), 219 (32), 77 (16), 73 (68), 57 (24), 56 (11), 43 (22), 41 (22). Found: C, 44.14; H, 6.07%. Calcd for $C_{13}H_{21}F_7OSi$: C, 44.06; H, 5.97%.

1,1,1,2-Tetrafluoro-2-trifluoromethyl-4-nonanone (18b): Bp 82–87 °C (45 Torr, bath temp); IR (neat) 2958, 2934, 1729, 1340, 1288, 1227, 1164, 1131, 1108, 996 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J*=6.7 Hz, 3H), 1.20–1.40 (m, 4H), 1.53–1.68 (m, 2H), 2.56 (t, *J*=7.1 Hz, 2H), 3.07 (d, *J*=21.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.66, 22.35, 22.94, 30.97, 40.33 (d, *J*=19.1 Hz), 44.44, 90.69 (dm,

J=208 Hz), 120.4 (qd, *J*=287, 27.8 Hz), 200.6; ^{19}F NMR ($CDCl_3$) δ -77.01 (d, *J*=7.3 Hz, 6F), -183.0 (tsep, *J*=22.0, 7.3 Hz, 1F); MS (70 eV) *m*/*z* (rel intensity) 282 (M^+, 7), 253 (5), 239 (15), 227 (21), 226 (100), 211 (36), 206 (6), 186 (3), 99 (5). Found: C, 42.83; H, 4.65%. Calcd for $C_{10}H_{13}F_7O$: C, 42.56; H, 4.64%.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-2-pentyl-1-triisopropylsiloxy-1-octene (20, Major): Stereochemistry (*E* or *Z*) could not be determined; Bp 92–97 °C (1 Torr, bath temp); IR (neat) 2948, 2868, 1659, 1466, 1240, 1145, 1112, 882, 708, 686, 653 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.7 Hz, 3H), 1.03–1.56 (m, 27H), 2.12–2.20 (m, 2H), 6.83 (t, *J*=2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.79, 13.97, 17.44, 22.49, 23.99, 28.53, 32.04, 111.1 (t, *J*=20.4 Hz), 146.4 (t, *J*=12.5 Hz); ^{19}F NMR ($CDCl_3$) δ -81.35 (t, *J*=9.8 Hz, 3F), -109.2– -109.6 (m, 2F), -122.1– -122.5 (m, 4F), -123.2 (bs, 2F), -126.4– -126.7 (m, 2F); MS (12 eV) *m*/*z* (rel intensity) 546 (M^+-^{i}Pr+1, 26), 545 (M^+-^{i}Pr, 100), 489 (4), 395 (3), 139 (2), 133 (3), 121 (2), 105 (2). Found: C, 45.18; H, 5.89%. Calcd for $C_{22}H_{33}F_{13}OSi$: C, 44.90; H, 5.65%.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-2-pentyl-1-triisopropylsiloxy-1-octene (20, Minor): Bp 105–110 °C (4 Torr, bath temp); IR (neat) 2950, 2868, 1656, 1466, 1281, 1240, 1202, 1146, 1130, 882, 808, 710, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.7 Hz, 3H), 1.00–1.50 (m, 27H), 1.98–2.05 (m, 2H), 6.59 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 11.67, 14.01, 17.37, 22.39, 27.78, 30.01, 31.27, 107.3 (t, *J*=20.3 Hz), 146.8 (t, *J*=5.7 Hz); ^{19}F NMR ($CDCl_3$) δ -81.32 (t, *J*=9.8 Hz, 3F), -108.9– -109.3 (m, 2F), -122.2– -122.7 (m, 4F), -123.3 (bs, 2F), -126.3– -126.8 (m, 2F); MS (12 eV) *m*/*z* (rel intensity) 546 (M^+-^{i}Pr+1, 26), 545 (M^+-^{i}Pr, 100), 489 (10), 395 (15), 157 (14), 133 (12), 121 (11), 105 (43), 77 (67), 43 (12). Found: C, 44.83; H, 5.54%. Calcd for $C_{22}H_{33}F_{13}OSi$: C, 44.90; H, 5.65%.

3,4,4,5,5,6,6,7,7,8,8,8-Dodecafluoro-2-pentyl-2-octenal (21, Major): Stereochemistry (*E* or *Z*) could not be determined; Bp 91–96 °C (27 Torr, bath

temp); IR (neat) 2960, 2932, 2866, 1697, 1658, 1361, 1301, 1237, 1201, 1166, 1145, 1113, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.7 Hz, 3H), 1.24–1.50 (m, 6H), 2.41–2.51 (m, 2H), 10.00 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.75, 22.23, 23.32 (d, *J*=3.8 Hz), 27.73, 31.46, 132.3 (d, *J*=9.1 Hz), 187.5 (d, *J*=8.3 Hz); ^{19}F NMR ($CDCl_3$) δ -81.25 (t, *J*=9.8 Hz, 3F), -107.1 (bs, 1F), -111.6 (bs, 2F), -123.3 (bs, 4F), -126.5 (bs, 2F); MS (12 eV) *m/z* (rel intensity) 412 (M^+, 7), 384 (23), 364 (19), 357 (34), 356 (53), 335 (50), 143 (100). Found: C, 38.03; H, 2.90%. Calcd for $C_{13}H_{12}F_{12}O$: C, 37.88; H, 2.93%.

3,4,4,5,5,6,6,7,7,8,8,8-Dodecafluoro-2-pentyl-2-octenal (21, Minor): Bp 88–93 °C (24 Torr, bath temp); IR (neat) 2960, 2934, 2874, 1700, 1660, 1362, 1237, 1205, 1144, 1113, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.23–1.46 (m, 6H), 2.26–2.34 (m, 2H), 10.23 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.77, 22.17 (two peaks), 29.21, 31.72, 129.3, 187.6 (d, *J*=18.8 Hz); ^{19}F NMR ($CDCl_3$) δ -81.26 (t, *J*=9.8 Hz, 3F), -115.6 (bs, 2F), -123.1 (bs, 4F), -126.2– -126.6 (m, 3F); MS (12 eV) *m/z* (rel intensity) 412 (M^+, 0.6), 335 (5), 145(11), 143 (100), 95 (7), 85 (24), 68 (8), 56 (24). Found: C, 37.58; H, 2.86%. Calcd for $C_{13}H_{12}F_{12}O$: C, 37.88; H, 2.93%.

The Reaction of Silyl Enolate with Trifluoromethyl Iodide in the Presence of Base. Typical procedure is as follows. CF_3I (2.88 g, 14.7 mmol) was introduced into the flask pre-cooled to -78 °C, then hexane (7.4 ml), silyl enolate (**22** (purity, 93%), 354 mg, 1.36 mmol), 2,6-dimethylpyridine (159mg, 1.47 mmol) and Et_3B (0.96 M hexane solution, 0.30 ml, 0.29 mmol) were slowly added to the flask. After addition of these reagents, the reaction mixture was warmed to room temperature and stirred for 40 h. The resulting precipitate was filtered through Celite 545 and the filtrate was concentrated *in vacuo*. Treatment of the crude product with concd aqueous HCl in THF and purification by silica-gel column chromatography gave **23a** in 64% yield.

1,1,1-Trifluoro-3-dodecanone (23a): Mp 44.5–45.5 °C; IR ($CDCl_3$) 2926, 2854, 1731, 1367, 1341, 1274, 1255, 1160, 1139 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.4 Hz, 3H), 1.27 (bs, 12H), 1.53–1.70 (m, 2H), 2.53 (t, *J*=7.3 Hz, 2H), 3.21 (q, *J*=10.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 22.63, 23.16, 28.90, 29.21, 29.31, 29.36, 31.83, 43.50, 46.18 (q, *J*=28.2 Hz), 123.7 (q, *J*=277 Hz), 200.2; ^{19}F NMR ($CDCl_3$) δ -62.91 (t, *J*=10.3 Hz); MS (12 eV) *m/z* (rel intensity) 238 (M^+, 12), 220 (23), 164 (26), 153 (26), 150 (34), 139 (32), 127 (30), 126 (88), 112 (100), 110 (46), 71 (25). Found: C, 60.72; H, 9.10%. Calcd for $C_{12}H_{21}F_3O$: C, 60.49; H, 8.88%.

5-Trifluoromethyl-6-undecanone (25a): Bp 79–84 °C (1 Torr, bath temp); IR (neat) 2958, 2932, 2870, 1729, 1261, 1163, 1123, 1091 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J*=6.8 Hz, 6H), 1.17–1.47 (m, 8H), 1.53–1.99 (m, 4H), 2.47 (dt, *J*=17.9, 7.1 Hz, 1H), 2.61 (dt, *J*=17.9, 7.3 Hz, 1H), 3.19 (dqd, *J*=9.2, 8.9, 4.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.59, 13.80, 22.39 (two peaks), 22.70, 25.61, 29.02, 31.07, 43.64, 55.56 (q, *J*=25.0 Hz), 124.9 (q, *J*=280 Hz), 204.4; ^{19}F NMR ($CDCl_3$) δ -67.33 (d, *J*=8.9 Hz); MS (12 eV) *m/z* (rel intensity) 238 (M^+, 3), 167 (4), 126 (5), 100 (7), 99 (100), 85 (4), 72 (4), 71 (19), 56 (6), 43 (7). Found: C, 60.20; H, 9.10%. Calcd for $C_{12}H_{21}F_3O$: C, 60.49; H, 8.88%.

The Reaction of Silyl Enolate with 2,2,2-Trifluoroethyl Iodide in the Presence of Base. The reactions were performed according to Procedure A' described for the reaction of silyl enolate with R_fI with some variation of the quantity of reagents and reaction time, which are shown below.

1,1,1-Trifluoro-4-tridecanone (23b). Et_3B (0.96 M hexane solution, 0.42 ml, 0.40 mmol) was added to a solution of silyl enolate (**22** (purity, 93%), 486mg, 1.86 mmol), CF_3CH_2I (840 mg, 4.00 mmol) and 2,6-dimethylpyridine (205 mg, 1.91 mmol) in hexane (5 ml) at room temperature. The resulting mixture was stirred for 15 h. Acidic work-up followed by purification gave **23b** in 79% yield:

Bp 90–95 °C (1 Torr, bath temp); IR (neat) 2926, 2854, 1723, 1442, 1364, 1315, 1256, 1231, 1143, 1091, 612 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.5 Hz, 3H), 1.27 (bs, 12H), 1.52–1.70 (m, 2H), 2.28–2.53 (m, 4H), 2.64–2.72 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.99, 22.61, 23.73, 27.86 (q, *J*=29.8 Hz), 29.11, 29.21, 29.32, 29.36, 31.82, 34.76 (q, *J*=2.7 Hz), 42.76, 127.0 (q, *J*=277 Hz), 207.1; ^{19}F NMR ($CDCl_3$) δ -67.17 (t, *J*=10.3 Hz); MS (12 eV) *m/z* (rel intensity) 252 (M^+, 9), 155 (66), 153 (16), 141 (29), 140 (100), 112 (37), 110 (21), 85 (15), 71 (28), 57 (20). Found: C, 62.04; H, 9.48%. Calcd for $C_{13}H_{23}F_3O$: C, 61.88; H, 9.19%.

5-(2,2,2-Trifluoroethyl)-6-undecanone (25b): Bp 65–70 °C (1 Torr, bath temp); IR (neat) 2956, 2930, 2862, 1719, 1467, 1459, 1378, 1257, 1131, 1102, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J*=6.8 Hz, 6H), 1.15–1.75 (m, 12H), 1.88–2.21 (m, 1H), 2.48 (t, *J*=7.5 Hz, 2H), 2.57–2.90 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.77, 13.88, 22.44, 22.54, 23.00, 28.79, 31.25, 31.82, 34.53 (q, *J*=28.4 Hz), 42.80, 44.93 (q, *J*=2.7 Hz), 126.6 (q, *J*=277 Hz), 211.5; ^{19}F NMR ($CDCl_3$) δ -65.50 (t, *J*=10.8 Hz); MS (12 eV) *m/z* (rel intensity) 252 (M^+, 3), 196 (8), 140 (7), 100 (6), 99 (100), 71 (15), 43 (4). Found: C, 62.04; H, 9.46%. Calcd for $C_{13}H_{23}F_3O$: C, 61.88; H, 9.19%.

The Reaction of 1-Trimethylsiloxy-1-cyclopropylethylene (26) with Perfluorohexyl or Perfluoroisopropyl Iodide. Perfluoroisopropylation of **26** is representative. Et_3B (1.0 M hexane solution, 0.20 ml, 0.20 mmol) was added to a solution of silyl enolate (0.16 g, 1.0 mmol) and *i*-C_3F_7I (0.50 g, 1.7 mmol) in hexane (2 ml). After stirring for 20 min, the reaction mixture was concentrated *in vacuo*. Purification by silica-gel column chromatography gave **27b** in 85% yield. Treatment of crude product with concd aqueous HCl in THF according to Procedure A' and purification by distillation gave **28b** in 83% yield.

(*Z*),(*E*)-6,7,7,7-Tetrafluoro-1-iodo-6-trifluoromethyl-4-trimethylsiloxy-3-heptene (27b, (*Z*):(*E*) = 81:19): Bp 92–97 °C (1 Torr, bath temp); IR (neat)

2960 , 1671, 1374, 1333, 1286, 1222, 1164, 1149, 1121, 1003, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.22 (s, 9H), 2.53 (dt, *J*=7.6, 7.0 Hz, 0.38H), 2.60 (td, *J*=7.4, 7.0 Hz, 1.62 H), 2.75 (d, *J*=21.6 Hz, 1.62H), 2.86 (d, *J*=21.0 Hz, 0.38H), 3.10 (t, *J*=7.4 Hz, 1.62H), 3.14 (t, *J*=7.0 Hz, 0.38H), 4.75 (t, *J*=7.0 Hz, 0.81H), 4.80 (t, *J*=7.6 Hz, 0.19H); ^{13}C NMR for (*Z*)-isomer ($CDCl_3$) δ 0.43, 4.00, 30.12, 35.99 (d, *J*=19.5 Hz), 91.41 (dm, *J*=207 Hz), 114.5, 120.9 (qd, *J*=288, 28.8 Hz), 142.4 (d, *J*=2.6 Hz); ^{13}C NMR for (*E*)-isomer ($CDCl_3$) δ -0.15, 5.92, 31.21, 31.49 (d, *J*=19.0 Hz), 111.0, 143.6 (d, *J*=3.4 Hz), (^{13}C of *i*-C_3F_7 could not be detected); ^{19}F NMR ($CDCl_3$) δ -76.56 (d, *J*=6.1 Hz, 4.86F), -76.79 (d, *J*=7.3 Hz, 1.14F), -182.1 (tsep, *J*=20.8, 7.3 Hz, 0.19F), -183.0 (tsep, *J*=22.0, 6.1 Hz, 0.81F); MS (70 eV) *m/z* (rel intensity) 452 (M^+, 2), 326 (18), 325 (100), 233 (8), 73 (18). Found: C, 29.16; H, 3.58%. Calcd for $C_{11}H_{16}F_7IOSi$: C, 29.22; 3.57%.

6,7,7,7-Tetrafluoro-1-iodo-6-trifluoromethyl-4-heptanone (28b): Bp 73–78 °C (1 Torr, bath temp); IR (neat) 1728, 1338, 1289, 1223, 1165, 1117, 1045, 1002 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.04–2.18 (m, 2H), 2.75 (t, *J*=7.0 Hz, 2H), 3.11 (d, *J*=21.9 Hz, 2H), 3.23 (t, *J*=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 5.31, 26.60, 40.55 (d, *J*=19.0 Hz), 44.69, 90.52 (dm, *J*=209 Hz), 120.3 (qd, *J*=288, 27.0 Hz), 199.1; ^{19}F NMR ($CDCl_3$) δ -76.98 (d, *J*=4.9 Hz, 6F), -182.8 (bs, 1F); MS (70 eV) *m/z* (rel intensity) 253 (M^+-I, 61), 211 (100), 155 (14), 95 (14), 69 (36), 42 (19), 41 (27). Found: C, 25.51; H, 2.29%. Calcd for $C_8H_8F_7IO$: C, 25.28; H, 2.12%.

6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluoro-1-iodo-4-undecanone (28a): Bp 100–105 °C (1 Torr, bath temp); IR (neat) 1729, 1345, 1241, 1209, 1146 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.07–2.20 (m, 2H), 2.78 (t, *J*=6.9 Hz, 2H), 3.22 (t, *J*=18.6 Hz, 2H), 3.25 (t, *J*=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 5.26, 26.52, 43.20 (t, *J*=22.1 Hz), 44.66, 198.4; ^{19}F NMR ($CDCl_3$) δ -81.45 (bs, 3F), -111.5 (bs, 2F), -122.2 (bs, 2F), -123.4 (bs, 4F), -126.7 (bs, 2F); MS (70 eV) *m/z* (rel intensity)

403 (M^+-I, 67), 362 (9), 361 (100), 341 (9), 197 (11), 169 (8), 155 (7), 69 (13), 41 (8). Found: C, 24.85; H, 1.52%. Calcd for $C_{11}H_8F_{13}IO$: C, 24.93; H, 1.52%.

The Reaction of 1-Trimethylsiloxy-1-cyclopropylethylene with Trifluoromethyl Iodide. CF_3I(0.40 ml, 5.0 mmol) was collected in the flask pre-cooled to -78 °C. Hexane (2 ml), silyl enolate (0.16 g, 1.0 mmol) and Et_3B (0.20 mmol) were added to CF_3I and the mixture was warmed to 5 °C over 3 h. After evaporation of solvent, the crude product was treated with concd aqueous HCl in THF. Purification by distillation gave **28c** in 67% yield: Bp 65–70 °C (1 Torr, bath temp); IR (neat) 1733, 1419, 1380, 1270, 1223, 1159, 1142, 1091, 626 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.05–2.18 (m, 2H), 2.72 (t, *J*=6.9 Hz, 2H), 3.24 (t, *J*=6.6 Hz, 2H), 3.26 (q, *J*=10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 5.55, 26.30, 43.59, 46.18 (q, *J*=28.3 Hz), 123.4 (q, *J*=277 Hz), 198.6; ^{19}F NMR ($CDCl_3$) δ -62.85 (t, *J*=9.8 Hz); MS (70 eV) *m/z* (rel intensity) 153 (M^+-I, 58), 127 (7), 111 (100), 91 (6), 83 (12), 42 (9), 41 (11), 39 (8). Found: C, 25.57; H, 2.79%. Calcd for $C_6H_8F_3IO$: C, 25.74; H, 2.88%.

Preparation of Ketene Silyl Acetals. The following ketene silyl acetals were prepared by the reported procedure.[9,16] The physical data for 1-hexyloxy-2-methyl-1-trimethylsiloxy-1-propene (**40**) is described in the literature.[17] The physical data for other compounds are shown below.

1-Butoxy-1-(*t*-butyldimethylsiloxy)ethylene (29): Bp 66–68 °C (2 Torr); IR (neat) 2958, 2930, 1653, 1277, 1254, 837, 784 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 6H), 0.93 (s, 9H), 0.94 (t, *J*=7.3 Hz, 3H), 1.33–1.52 (m, 2H), 1.59–1.72 (m, 2H), 3.06 (d, *J*=2.3 Hz, 1H), 3.22 (d, *J*=2.3 Hz, 1H), 3.68 (t, *J*=6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -4.56, 13.73, 18.09, 19.31, 25.62, 30.95, 60.32, 67.48, 161.5; MS (70 eV) *m/z* (rel intensity) 230 (M^+, 9), 174 (14), 159 (13), 131 (78), 117 (91), 75 (100), 73 (67), 57 (15), 43 (14), 41 (23). Found: C, 62.27; H, 11.62%. Calcd for $C_{12}H_{26}O_2Si$: C, 62.55; H, 11.37%.

1-(*t*-Butyldimethylsiloxy)-1-octyloxyethylene (32): Bp 114–117 °C (2 Torr); IR (neat) 2954, 2928, 2856, 1651, 1276, 1254, 829, 785 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 6H), 0.89 (t, *J*=6.6 Hz, 3H), 0.93 (s, 9H), 1.28 (bs, 10H), 1.60–1.73 (m, 2H), 3.05 (d, *J*=2.3 Hz, 1H), 3.22 (d, *J*=2.3 Hz, 1H), 3.67 (t, *J*=6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -4.54, 14.07, 18.13, 22.65, 25.63, 26.11, 28.89, 29.22 (two peaks), 31.80, 60.32, 67.78, 161.5; MS (70 eV) *m/z* (rel intensity) 286 (M^+, 2), 187 (28), 175 (18), 119 (17), 117 (100), 75 (67), 73 (44), 43 (23). Found: C, 67.23; H, 12.23%. Calcd for $C_{16}H_{34}O_2Si$: C, 67.07; H, 11.96%.

1-Butoxy-1-(trimethylsiloxy)ethylene (34): Bp 95–101 °C (39 Torr); IR (neat) 2960, 1657, 1278, 1252, 1088, 1023, 849, 757 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.22 (s, 9H), 0.94 (t, *J*=7.2 Hz, 3H), 1.34–1.52 (m, 2H), 1.60–1.73 (m, 2H), 3.06 (d, *J*=2.5 Hz, 1H), 3.21 (d, *J*=2.5 Hz, 1H), 3.70 (t, *J*=6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 0.05, 13.69, 19.26, 30.91, 60.03, 67.54, 161.2; MS (70 eV) *m/z* (rel intensity) 188 (M^+, 3), 131 (26), 117 (94), 75 (100), 73 (97), 72 (23), 57 (22), 56 (41), 45 (26), 43 (80), 41 (43). Found: C, 57.20; H, 10.91%. Calcd for $C_9H_{20}O_2Si$: C, 57.40; H, 10.70%.

1-(Trimethylsiloxy)-1-octyloxyethylene (35): Bp 91–96 °C (1 Torr); IR (neat) 2956, 2926, 2854, 1656, 1277, 1252, 1019, 848 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.22 (s, 9H), 0.88 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.60–1.73 (m, 2H), 3.05 (d, *J*=2.5 Hz, 1H), 3.20 (d, *J*=2.5 Hz, 1H), 3.68 (t, *J*=6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 0.08, 14.03, 22.62, 26.09, 28.87, 29.22 (two peaks), 31.78, 60.03, 67.85, 161.2; MS (70 eV) *m/z* (rel intensity) 244 (M^+, 2), 187 (20), 133 (42), 117 (100), 75 (43), 73 (48), 56 (21), 43 (51), 41 (23). Found: C, 63.62; H, 11.51%. Calcd for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.55%.

1-Methoxy-1-(trimethylsiloxy)-1-hexene (36, (*E*):(*Z*) = 83:17): Bp 102–105 °C (36 Torr); IR (neat) 2956, 1682, 1254, 1227, 1174, 1089, 906, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 1.53H), 0.23 (s, 7.47H), 0.89 (t, *J*=6.8 Hz, 3H),

1.25–1.40 (m, 4H), 1.90–2.01 (m, 2H), 3.47 (t, *J*=6.8 Hz, 0.17), 3.48 (s, 0.51H), 3.52 (s, 2.49H), 3.67 (t, *J*=7.1 Hz, 0.83H); ^{13}C NMR for (*E*)-isomer ($CDCl_3$) δ -0.32, 13.92, 22.20, 24.10, 32.91, 54.76, 85.33, 153.5; MS (70 eV) *m/z* (rel intensity) 202 (M^+, 8), 159 (47), 89 (19), 73 (58), 59 (11), 55 (100), 45 (11). Found: C, 59.47; H, 11.22%. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96%.

1-Methoxy-1-(trimethylsiloxy)-1-octene (38, (*E*):(*Z*) = 88:12): Bp 68–70 °C (1 Torr); IR (neat) 2956, 2922, 2852, 1682, 1253, 1227, 1170, 1091, 902, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 1.08H), 0.23 (s, 7.92H), 0.88 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 8H), 1.89–2.03 (m, 2H), 3.47 (t, *J*=6.8 Hz, 0.12H), 3.48 (s, 0.36H), 3.51 (s, 2.64H), 3.67 (t, *J*=7.3 Hz, 0.88H); ^{13}C NMR for (*E*)-isomer ($CDCl_3$) δ -0.30, 14.07, 22.68, 24.43, 28.85, 30.67, 31.78, 54.78, 85.42, 153.5; MS (70 eV) *m/z* (rel intensity) 230 (M^+, 10), 160 (11), 159 (75), 89 (16), 73 (52), 59 (11), 55 (100), 41 (11). Found: C, 62.68; H, 11.63%. Calcd for $C_{12}H_{26}O_2Si$: C, 62.55; H, 11.37%.

1-(3-Butenyloxy)-1-(trimethylsiloxy)ethylene (42): Bp 90–91 °C (39 Torr); IR (neat) 2958, 1653, 1277, 1253, 1088, 1018, 990, 911, 847, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.22 (s, 9H), 2.43 (qt, *J*=6.7, 1.3 Hz, 2H), 3.07 (d, *J*=2.6 Hz, 1H), 3.23 (d, *J*=2.6 Hz, 1H), 3.75 (t, *J*=6.7 Hz, 2H), 5.08 (ddt, *J*=10.2, 1.8, 1.3 Hz, 1H), 5.13 (ddt, *J*=17.0, 1.8, 1.3 Hz, 1H), 5.84 (ddd, *J*=17.0, 10.2, 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.09, 33.28, 60.26, 67.00, 117.0, 134.4, 161.0; MS (70 eV) *m/z* (rel intensity) 186 (M^+, 3), 101 (21), 75 (61), 73 (100), 55 (73), 54 (85), 43 (45). Found: C, 57.74; H, 9.82%. Calcd for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74%.

The Reaction of 1-Butoxy-1-(*t*-butyldimethylsiloxy)ethylene with Perfluorohexyl Iodide in the Presence of 2,6-Dimethylpyridine (Procedure A). This reaction gave a mixture of **30a** and **31** in 37% and 10% yield respectively. Butyl 3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctanoate (**30a**): Bp 76–81 °C (7 Torr, bath temp); IR (neat) 2964, 1754, 1396, 1353, 1241, 1208, 1146, 1122, 1064, 709, 628 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, *J*=7.2 Hz, 3H), 1.31–1.49 (m, 2H),

1.57–1.73 (m, 2H), 3.14 (t, *J*=17.7 Hz, 2H), 4.20 (t, *J*=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.53, 18.94, 30.37, 37.02 (t, *J*=22.5 Hz), 65.91, 163.9; ^{19}F NMR ($CDCl_3$) δ -81.34 (tt, *J*=7.4, 3.0 Hz, 3F), -111.6– -112.6 (m, 2F), -112.1 (bs, 2F), -123.4 (bs, 4F), -126.3– -126.8 (m, 2F); MS (70 eV) *m/z* (rel intensity) 434 (M^+, 0.2), 361 (26), 69 (18), 57 (42), 56 (100), 55 (12), 41 (35). Found: C, 33.45; H, 2.46%. Calcd for $C_{12}H_{11}F_{13}O_2$: C, 33.20; H, 2.55%. (*E*)-Butyl 3,4,4,5,5,6,6,7,7,8,8,8-Dodecafluoro-2-octenoate (**31**): Bp 83–88 °C (13 Torr, bath temp); IR (neat) 2964, 1736, 1702, 1350, 1275, 1239, 1206, 1143, 1114, 723, 644 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (t, *J*=7.3 Hz, 3H), 1.33–1.51 (m, 2H), 1.60–1.76 (m, 2H), 4.24 (t, *J*=6.6 Hz, 2H), 6.00 (d, *J*=29.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.45, 19.02, 30.44, 65.64, 107.2 (t, *J*=4.0 Hz), 161.6 (d, *J*=2.7 Hz); ^{19}F NMR ($CDCl_3$) δ -81.14– -81.43 (m, 3F), -107.7– -108.7 (m, 1F), -118.9– -119.4 (m, 2F), -123.2 (bs, 4F), -126.6 (bs, 2F); MS (12 eV) *m/z* (rel intensity) 359 (M^+-C_4H_7, 6), 341 (5), 57 (5), 56 (100), 55 (2). Found: C, 35.02; H, 2.49%. Calcd for $C_{12}H_{10}F_{12}O_2$: C, 34.80; H, 2.43%.

The Reactions of Ketene Silyl Acetals with Perfluorohexyl Iodide without Base (Procedure B). Following procedure for the reaction of ketene *t*-butyldimethylsilyl acetal derived from butyl acetate with *n*-$C_6F_{13}I$ is typical. Under argon atmosphere, Et_3B was added to a solution of ketene silyl acetal (**29**, 456 mg, 1.98 mmol) and *n*-$C_6F_{13}I$ (440 mg, 0.99 mmol) in hexane (4.9 ml). After stirring for 10 min, saturated aqueous $NaHCO_3$ (5 ml) was added to the reaction mixture. The mixture was vigorously stirred for 40 min, then poured into water (30 ml) and extracted with hexane (30 mL x 2). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residual oil was purified by silica-gel column chromatography to give **30a** in 87% yield.

Methyl 2-Butyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoate (37a): Bp 98–103 °C (20 Torr, bath temp); IR (neat) 2964, 2936, 2870, 1757, 1458, 1437,

1350, 1239, 1194, 1145, 1116, 712, 695, 652 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, *J*=6.8 Hz, 3H), 1.21–1.47 (m, 4H), 1.74–2.07 (m, 2H), 3.06–3.29 (m, 1H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 13.42, 22.19, 24.87, 28.98, 48.15 (dd, *J*=22.6, 20.6 Hz), 52.28, 168.1 (d, *J*=7.8 Hz); ^{19}F NMR ($CDCl_3$) δ -81.32 (t, *J*=9.8 Hz, 3F), -113.7 (dm, *J*=266 Hz, 1F), -116.4 (dm, *J*=266 Hz, 1F), -121.8– -122.4 (m, 4F), -123.3 (bs, 2F), -126.3– -126.9 (m, 2F); MS (70 eV) *m/z* (rel intensity) 448 (M^+, 0.1), 392 (11), 129 (16), 123 (100), 91 (13), 88 (14), 87 (12), 69 (14), 59 (68), 57 (11), 55 (24), 43 (13), 42 (14), 41 (21). Found: C, 34.82; H, 2.84%. Calcd for $C_{13}H_{13}F_{13}O_2$: C, 34.84; H, 2.92%.

Hexyl 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-2,2-dimethyl-octanoate (41a): Bp 69–74 °C (2 Torr, bath temp); IR (neat) 2960, 2932, 2862, 1746, 1477, 1277, 1241, 1195, 1177, 1147, 1112, 1063, 697, 658 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.23–1.42 (m, 6H), 1.46 (s, 6H), 1.57–1.71 (m, 2H), 4.14 (t, *J*=6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.74, 19.99, 22.48, 25.46, 28.29, 31.34, 48.48 (t, *J*=20.8 Hz), 66.02, 170.6 (t, *J*=3.1 Hz); ^{19}F NMR ($CDCl_3$) δ -81.33 (tt, *J*=9.9, 2.5 Hz, 3F), -114.7 (bs, 2F), -118.1 (bs, 2F), -112.4 (bs, 2F), -123.1 (bs, 2F), -126.3– -126.8 (m, 2F); MS (12 eV) *m/z* (rel intensity) 407 (M^+-C_6H_{11}, 15), 85 (49), 84 (100), 69 (9), 57 (11), 56 (37), 43 (51). Found: C, 39.22; H, 3.89%. Calcd for $C_{16}H_{19}F_{13}O_2$: C, 39.20; H, 3.91%.

The Reaction of Ketene Silyl Acetals with Perfluoroisopropyl Iodide. Et_3B (0.2 mmol) was added to a solution of ketene silyl acetal (2.0 mmol) and *i*-C_3F_7I (1.0 mmol) in hexane (5 ml) at 0 °C. After an addition of Et_3B, the reaction mixture was immediately warmed up to room temperature and stirred for appropriate time given in Table 3. Work-up and purification were performed according to Procedure B. In the case of ketene trimethylsilyl acetals **34** or **35**, butyl or octyl 2-(trimethylsilyl)acetate was obtained as by-product. These trimethylsilylacetates could be produced by isomerization of starting ketene acetals

34 and **35** under the reaction conditions. Tetrabutylammonium fluoride (TBAF, 1.0 mmol per 1.0 mmol of ketene silyl acetal) was added to the reaction mixture prior to work-up to remove these by-products from perfluoroalkylated esters **30** and **33**. Thus, TBAF was added and the resulting mixture was stirred for 10 min at room temperature. The resulting mixture was poured into aqueous NH_4Cl (saturated aqueous NH_4Cl:water = 1:10). Extraction and purification by silica-gel column chromatography provided the desired perfluoroalkylated esters.

Butyl 3,4,4,4-Tetrafluoro-3-trifluoromethylbutanoate (30b): Bp 68–73 °C (36 Torr, bath temp); IR (neat) 2962, 1753, 1346, 1296, 1229, 1202, 1168, 1129, 1060, 1004, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, *J*=7.1 Hz, 3H), 1.30–1.48 (m, 2H), 1.57–1.71 (m, 2H), 3.07 (d, *J*=20.4 Hz, 2H), 4.17 (t, *J*=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.46, 18.91, 30.26, 34.21 (d, *J*=19.8 Hz), 65.96, 89.98 (dm, *J*=211 Hz), 120.4 (qd, *J*=288, 27.9 Hz), 164.4 (d, *J*=2.5 Hz); ^{19}F NMR ($CDCl_3$) δ -77.25 (d, *J*=7.3 Hz, 6F), -182.9 (tsep, *J*=20.1, 7.3 Hz, 1F); MS (70 eV) *m/z* (rel intensity) 284 (M^+, 0.6), 255 (3), 229 (5), 212 (6), 211 (100), 191 (2), 163 (2), 56 (3). Found: C, 38.26; H, 3.94%. Calcd for $C_9H_{11}F_7O_2$: C, 38.04; H, 3.90%.

Octyl 3,4,4,4-Tetrafluoro-3-trifluoromethylbutanoate (33a): Bp 69–74 °C (1 Torr, bath temp); IR (neat) 2958, 2930, 2860, 1754, 1347, 1296, 1230, 1202, 1169, 1061, 1006, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.59–1.73 (m, 2H), 3.06 (d, *J*=20.4 Hz, 2H), 4.16 (t, *J*=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.94, 22.60, 25.69, 28.26, 29.11 (two peaks), 31.75, 34.22 (d, *J*=19.9 Hz), 66.24, 89.99 (dm, *J*=211 Hz), 120.4 (qd, *J*=288, 28.2 Hz), 164.4; ^{19}F NMR ($CDCl_3$) δ -77.23 (d, *J*=6.9 Hz, 6F), -182.9 (tsep, *J*=20.2, 6.9 Hz, 1F); MS (12 eV) *m/z* (rel intensity) 229 (M^+-C_8H_{15}, 12), 112 (55), 84 (100), 83 (81), 82 (30), 70 (84), 69 (34), 68 (29), 56 (52). Found: C, 46.06; H, 5.81%. Calcd for $C_{13}H_{19}F_7O_2$: C, 45.89; H, 5.63%.

Methyl 2-(Perfluoroisopropyl)hexanoate (37b): Bp 78–83 °C (50 Torr,

bath temp); IR (neat) 2962, 2934, 2878, 1757, 1460, 1439, 1282, 1222, 1169, 1135, 1111, 1092, 984, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, *J*=7.0 Hz, 3H), 1.15–1.50 (m, 4H), 1.69–1.86 (m, 1H), 1.91–2.12 (m, 1H), 3.10–3.24 (m, 1H), 3.77 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 13.56, 22.12, 25.44, 29.84, 46.90 (d, *J*=20.1 Hz), 52.51, 91.53 (dm, *J*=208 Hz), 120.7 (qd, *J*=289, 29.9 Hz), 168.3 (d, *J*=6.0 Hz); ^{19}F NMR ($CDCl_3$) δ -74.04 (d, *J*=7.3 Hz, 6F), -178.6 (dsep, *J*=12.2, 6.1 Hz, 1F); MS (70 eV) *m/z* (rel intensity) 298 (M^+, 0.2), 267 (23), 255 (21), 242 (80), 173 (100), 141 (11), 129 (18), 59 (13). Found: C, 40.25; H, 4.54%. Calcd for $C_{10}H_{13}F_7O_2$: C, 40.28; H, 4.39%.

Methyl 2-(Perfluoroisopropyl)octanoate (39a): Bp 85–90 °C (24 Torr, bath temp); IR (neat) 2958, 2930, 2860, 1757, 1459, 1439, 1302, 1229, 1168, 1134, 1114, 1093, 976, 718 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 8H), 1.67–1.89 (m, 1H), 1.92–2.13 (m, 1H), 3.09–3.23 (m, 1H), 3.77 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 13.77, 22.41, 25.69, 27.67, 28.64, 31.38, 46.90 (d, *J*=20.2 Hz), 52.39, 91.48 (dm, *J*=209 Hz), 120.6 (qd, *J*=287, 27.0 Hz), 168.0–168.2 (m); ^{19}F NMR ($CDCl_3$) δ -74.03 (d, *J*=6.1 Hz, 6F), -178.7 (dsep, *J*=13.4, 6.1 Hz, 1F); MS (70 eV) *m/z* (rel intensity) 326 (M^+, 2), 297 (25), 295 (13), 255 (58), 242 (100), 173 (91), 59 (17), 55 (14), 43 (17), 41 (16). Found: C, 43.96; H, 5.27%. Calcd for $C_{12}H_{17}F_7O_2$: C, 44.18; H, 5.25%.

Hexyl 3,4,4,4-Tetrafluoro-2,2-dimethyl-3-trifluoromethylbutanoate (41b): Bp 72–77 °C (3 Torr, bath temp); IR (neat) 2958, 2932, 2860, 1743, 1472, 1287, 1228, 1190, 1166, 1149, 1116, 1033, 995, 726 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J*=6.6 Hz, 3H), 1.26–1.45 (m, 6H), 1.50 (s, 6H), 1.58–1.74 (m, 2H), 4.12 (t, *J*=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.84, 21.23, 22.46, 25.44, 28.15, 31.29, 46.54 (d, *J*=19.0 Hz), 66.23, 93.87 (dm, *J*=216 Hz), 121.2 (qd, *J*=289, 28.7 Hz), 171.4; ^{19}F NMR ($CDCl_3$) δ -70.76 (d, *J*=4.9 Hz, 6F), -178.0 (bs, 1F); MS (12 eV) *m/z* (rel intensity) 257 (M^+-C_6H_{11}, 27), 85 (65), 84 (62), 69 (11), 57 (24), 56 (32), 43

(100). Found: C, 45.93; H, 5.81%. Calcd for $C_{13}H_{19}F_7O_2$: C, 45.89; H, 5.63%.

The Reaction of Ketene Silyl Acetals with Trifluoromethyl Iodide. CF_3I (1.0 mmol) was introduced into the flask pre-cooled to -78 °C, then hexane (5.0 ml) and ketene silyl acetal (2.0 mmol) were added to the flask. Et_3B (0.2 mmol) was added and the reaction mixture was immediately warmed up to room temperature. After stirring for several hours (Table 3), extractive work-up followed by purification gave the corresponding trifluoromethylated ester.

Octyl 3,3,3-Trifluoropropanoate (33b): Bp 56–61 °C (1 Torr, bath temp); IR (neat) 2956, 2926, 2856, 1754, 1418, 1399, 1364, 1269, 1221, 1119 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.59–1.74 (m, 2H), 3.17 (q, *J*=10.1 Hz, 2H), 4.18 (t, *J*=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.01, 22.60, 25.69, 28.34, 29.09 (two peaks), 31.72, 39.66 (q, *J*=30.9 Hz), 65.95, 123.4 (q, *J*=277 Hz), 164.1 (q, *J*=4.2 Hz); ^{19}F NMR ($CDCl_3$) δ -64.02 (t, *J*=10.4 Hz); MS (70 eV) *m/z* (rel intensity) 129 (M^+-C_8H_{15}, 6), 112 (23), 84 (94), 83 (73), 70 (100), 69 (45), 68 (30), 56 (73). Found: C, 55.21; H, 8.13%. Calcd for $C_{11}H_{19}F_3O_2$: C, 54.99; H, 7.97%.

Methyl 2-Trifluoromethyloctanoate (39b): Bp 78–83 °C (24 Torr, bath temp); IR (neat) 2956, 2928, 2860, 1755, 1459, 1439, 1354, 1272, 1209, 1165, 1126, 1107 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1.21–1.41 (m, 8H), 1.67–2.01 (m, 2H), 3.11 (dqd, *J*=9.9, 8.4, 4.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 13.87, 22.44, 26.11, 26.70, 28.74, 31.37, 50.28 (q, *J*=27.4 Hz), 52.44, 124.7 (q, *J*=280 Hz), 168.2 (q, *J*=2.7 Hz); ^{19}F NMR ($CDCl_3$) δ -68.86 (d, *J*=8.5 Hz); MS (12 eV) *m/z* (rel intensity) 226 (M^+, 0.3), 155 (23), 143 (13), 142 (100), 116 (27), 115 (18), 85 (27), 84 (16). Found: C, 53.05; H, 7.82%. Calcd for $C_{10}H_{17}F_3O_2$: C, 53.09; H, 7.57%.

Hexyl 3,3,3-Trifluoro-2,2-dimethylpropanoate (41c): Bp 58–63 °C (5 Torr, bath temp); IR (neat) 2956, 2932, 2860, 1745, 1476, 1401, 1282, 1206, 1152, 1119

cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.6 Hz, 3H), 1.24–1.39 (m, 6H), 1.42 (s, 6H), 1.58–1.73 (m, 2H), 4.16 (t, *J*=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.87, 19.67, 22.46, 25.36, 28.32, 31.28, 48.45 (q, *J*=25.5 Hz), 65.84, 126.4 (q, *J*=282 Hz), 170.5; ^{19}F NMR ($CDCl_3$) δ -75.42 (s); MS (12 eV) *m/z* (rel intensity) 157 (M^+-C_6H_{11}, 31), 139 (8), 85 (32), 84 (100), 69 (24), 57 (13), 56 (68), 43 (50), 42 (9). Found: C, 55.09; H, 8.18%. Calcd for $C_{11}H_{19}F_3O_2$: C, 54.99; H, 7.97%.

The Reaction of Ketene Silyl Acetals with 2,2,2-Trifluoroethyl Iodide. The reactions were performed according to Procedure B.

Octyl 4,4,4-Trifluorobutanoate (33c): Bp 72–77 °C (1 Torr, bath temp); IR (neat) 2958, 2928, 2858, 1744, 1332, 1265, 1230, 1192, 1145, 1112, 985 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.30 (bs, 10H), 1.57–1.71 (m, 2H), 2.33–2.63 (m, 4H), 4.11 (t, *J*=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.99, 22.60, 25.83, 27.09 (q, *J*=3.3 Hz), 28.50, 29.14 (two peaks), 29.35 (q, *J*=29.6 Hz), 31.74, 65.26, 126.5 (q, *J*=277 Hz), 170.9; ^{19}F NMR ($CDCl_3$) δ -67.56 (t, *J*=10.4 Hz); MS (12 eV) *m/z* (rel intensity) 143 (M^+-C_8H_{15}, 27), 112 (44), 84 (96), 83 (83), 82 (24), 70 (100), 69 (36), 68 (23), 56 (59). Found: C, 56.84; H, 8.61%. Calcd for $C_{12}H_{21}F_3O_2$:, C, 56.68; H, 8.32%.

Methyl 2-(2,2,2-Trifluoroethyl)octanoate (39c): Bp 88–93 °C (24 Torr, bath temp); IR (neat) 2954, 2928, 2858, 1744, 1438, 1381, 1260, 1203, 1153, 1126, 1096 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.5 Hz, 3H), 1.27 (bs, 8H), 1.45–1.77 (m, 2H), 2.05–2.33 (m, 1H), 2.47–2.77 (m, 2H), 3.72 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.49, 26.68, 28.86, 31.51, 32.52, 35.87 (q, *J*=29.1 Hz), 39.34, 51.96, 126.2 (q, *J*=277 Hz), 174.6; ^{19}F NMR ($CDCl_3$) δ -65.93 (t, *J*=10.4 Hz); MS (70 eV) *m/z* (rel intensity) 240 (M^+, 0.9), 169 (18), 156 (100), 87 (42), 59 (22), 57 (11), 55 (18), 43 (18), 41 (21). Found: C, 54.70; H, 8.18%. Calcd for $C_{11}H_{19}F_3O_2$: C, 54.99; H, 7.97%.

The Reaction of 42 with Perfluorohexyl Iodide. Following the

procedure B, treatment of ketene silyl acetal **42** with *n*-$C_6F_{13}I$ provided a cyclized product **43** (10%) and perfluoroalkylated ester **44** (50%). 3-Iodomethyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-2-(trimethylsiloxy)oxolane (**43**): Bp 93–98 °C (1 Torr, bath temp); IR (neat) 2956, 2894, 1363, 1234, 1146, 1123, 1018, 908, 845, 719, 709, 634 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 (s, 9H), 1.73–1.94 (m, 1H), 2.28–2.76 (m, 4H), 3.04 (dd, *J*=10.2, 9.9 Hz, 1H), 3.38 (dd, *J*=9.9, 4.2 Hz, 1H), 3.81 (ddd, *J*=10.6, 8.6, 6.2 Hz, 1H), 4.01 (ddd, *J*=8.6, 8.3, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.06, 3.54, 32.86, 39.10 (t, *J*=20.0 Hz), 51.10, 65.81, 103.7; ^{19}F NMR ($CDCl_3$) δ -81.31 (tt, *J*=9.8, 3.0 Hz, 3F), -112.7– -114.1 (m, 2F), -122.1 (bs, 2F), -123.4 (bs, 2F), -124.0 (bs, 2F), -126.3– -126.8 (m, 2F); MS (12 eV) *m/z* (rel intensity) 632 (M^+, 0.1), 618 (12), 506 (21), 505 (100), 489 (8), 304 (6), 303 (49), 299 (15), 55 (54). Found: C, 28.72; H, 2.96%. Calcd for $C_{15}H_{18}F_{13}IO_2Si$: C, 28.49; H, 2.87%. 3-Butenyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoate (**44**): Bp 91–96 °C (27 Torr, bath temp); IR (neat) 1755, 1352, 1241, 1207, 1145, 1122, 709, 628 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.43 (qt, *J*=6.7, 1.3 Hz, 2H), 3.14 (t, *J*=17.5 Hz, 2H), 4.26 (t, *J*=6.7 Hz, 2H), 5.11 (ddt, *J*=10.2, 1.7, 1.3 Hz, 1H), 5.13 (ddt, *J*=17.1, 1.7, 1.3 Hz, 1H), 5.78 (ddt, *J*=17.1, 10.2, 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 32.81, 36.92 (t, *J*=22.5 Hz), 64.99, 117.5, 133.3, 163.8; ^{19}F NMR ($CDCl_3$) δ -81.31 (tt, *J*=6.9, 3.0 Hz, 3F), -111.6– -112.5 (m, 2F), -122.2 (bs, 2F), -123.3 (bs, 4F), -126.3– -126.8 (m, 2F); MS (12 eV) *m/z* (rel intensity) 432 (M^+, 2), 362 (9), 361 (100), 341 (16), 55 (5), 54 (93). Found: C, 33.49; H, 2.23%. Calcd for $C_{12}H_9F_{13}O_2$: C, 33.35; H, 2.10%.

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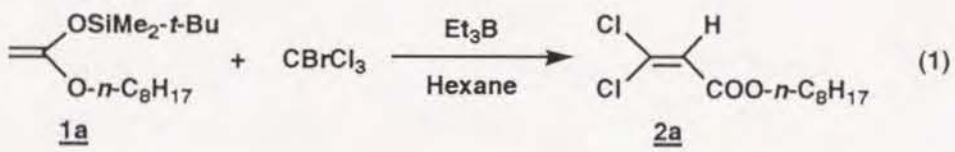
CHAPTER 4

Triethylborane Induced Radical Reaction of Ketene Silyl Acetals with Polyhalomethanes

The treatment of ketene silyl acetal with tetrahalomethane or trihalomethane at room temperature in the presence of a catalytic amount of Et_3B provides 3,3-dihaloacrylate or (*E*)-3-haloacrylate, respectively. On the other hand, a reaction at -23 °C mainly gives 3,3,3-trihalopropanoate or 3,3-dihalopropanoate.

The addition of alkyl radicals to alkenes is one of the most important methodologies for synthesizing aliphatic C-C bonds via radical reactions. Recently, the development of a more efficient inter- or intramolecular radical addition has been the object of research in many laboratories.[1] Previously, we reported[2] that Et_3B[3] induced a radical addition of perfluoroalkyl iodides to ketone silyl enol ether, giving 2-perfluoroalkylated ketones. Ketene silyl acetals are more electron-rich olefins than ketone silyl enol ethers, and are good acceptors of electrophilic carbon radicals, such as perfluoroalkyl radicals.[2] Described herein is a further exploitation of this method regarding the reaction of polyhalomethanes[4] with ketene silyl acetals.[5]

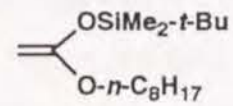
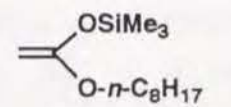
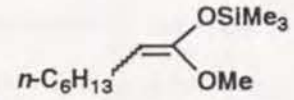
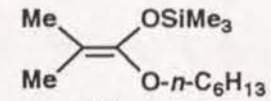
(1) Reaction of Ketene Silyl Acetals with Tetrahalomethanes. The reaction of ketene silyl acetal (**1a**, 2.0 mmol) with $CBrCl_3$ (1.0 mmol) at room temperature in the presence of Et_3B (0.2 mmol) gave octyl 3,3-dichloroacrylate (**2a**) in 93% yield (eq 1).

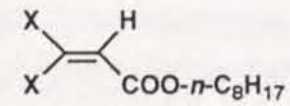


(1)

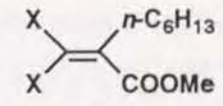
Not only $CBrCl_3$, but also CX_4 (X = Cl, Br, I) or CF_2Br_2 easily reacted with **1a** to afford the corresponding octyl 3,3-dihaloacrylate **2a**, **2b**, **2d**, or **2c** (Table 1).[6] In the case of CF_2Br_2 (Entry 4 in Table 1), octyl 3-bromo-3,3-difluoropropanoate (**3c**) was obtained in 5% yield as a by-product, along with **2c**. The use of ketene trimethylsilyl acetal (**1b**) instead of **1a** slightly increased the ratio of product **3** to **2**.

Table 1. Reaction of Ketene Silyl Acetal with Tetrahalomethane[a]

Entry	Ketene silyl acetal	Tetrahalomethane	Reaction time /h	Product (Yield / %)[b] 2	3
1	 1a	$CBrCl_3$	0.5	**2a** (93)	**3a** (0)
2		CCl_4	1.5	**2a** (79)	**3a** (0)
3		CBr_4	3	**2b** (90)	**3b** (0)
4		CF_2Br_2	0.5	**2c** (84)	**3c** (5)
5		CI_4	1	**2d** (40)	**3d** (0)[c]
6	 1b	$CBrCl_3$	0.5	**2a** (78)	**3a** (4)
7		CCl_4	1.5	**2a** (71)	**3a** (2)
8		CBr_4	3	**2b** (87)	**3b** (0)
9		CF_2Br_2	0.5	**2c** (74)	**3c** (10)
10	 1c	$CBrCl_3$	2	**2e** (0)	**3e** (90)
11		CCl_4	12	**2e** (0)	**3e** (56)
12		CBr_4	12	**2f** (21)	**3f** (44)[d]
13		CF_2Br_2	2	**2g** (2)	**3g** (86)
14	 1d	$CBrCl_3$	12	- -	**3i** (46)



2a: X=Cl, **2b**: X=Br, **2c**: X=F, **2d**: X=I



2e: X=Cl, **2f**: X=Br, **2g**: X=F

X_3CCH_2COO-*n*-C_8H_{17}
3a: X=Cl, **3b**: X=Br, **3d**: X= I

$X_3CCH(n\text{-}C_6H_{13})COOMe$
3e: X=Cl, **3f**: X=Br

$Cl_3CC(Me)_2COO$-*n*-C_6H_{13}
3i

F_2BrCCH_2COO-*n*-C_8H_{17}
3c

$F_2BrCCH(n\text{-}C_6H_{13})COOMe$
3g

a) Ketene silyl acetal (2.0 mmol), tetrahalomethane (1.0 mmol), and Et_3B (0.2 mmol), were employed. b) Yields based on tetrahalomethane. Entry1-3, 8, 10, 11 and 14 : Isolated yields. Entry 4-7, 9, 12 and 13 : Yields are determined by the examination of ^{1}H-NMR of the mixture of **2**, **3** and another product (Entry 5, 12) after purification. c) Octyl (*E*)-3-iodoacrylate (**4d**) was also obtained in 17% yield along with **2d**. d) Methyl 2-(dibromomethyl)octanoate (**5f**) was obtained in 4% yield in addition to **2f** and **3f**.

Table 2. Reaction of Ketene Silyl Acetal with $CBrCl_3$ under Various Conditions[a)]

Entry	Ketene silyl acetal / mmol	Reaction temp / °C	Reaction time / h	Yield /%[b)] **2a**	**3a**
1	**1a** (2.0)	r.t.	0.5	93	0
2	**1a** (2.0)	-23	1	37	58
3	**1a** (2.0)	-78	8[c)]	5	55
4	**1a** (1.0)	-23	1	32	19
5	**1b** (2.0)	r.t.	0.5	78	4
6	**1b** (2.0)	-23	1	5	91
7	**1b** (2.0)	-78	8[c)]	<1	54
8	**1b** (1.0)	-23	1	5	64
9	**1b** (1.5)	-23	1	7	91

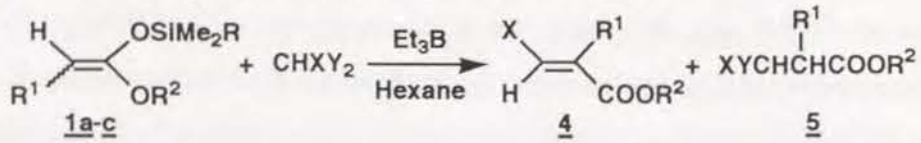
a) Ketene silyl acetal (1.0-2.0 mmol), $CBrCl_3$ (1.0 mmol), and Et_3B (0.2 mmol) were employed. b) Yields were determined by the examination of ^{1}H NMR of the mixture of **2a** and **3a** after purification. c) The reaction was stopped by the addition of galvinoxyl (0.0025 mmol) after stirring for 8 h.

The distribution of products **2** and **3** heavily depends on the reaction temperature (Table 2). Whereas the reaction of **1a** with $CBrCl_3$ at room temperature provided **2a** exclusively, the reaction at -23 °C gave **3a** as a major product (**2a**:**3a** = 39:61). At -78 °C, the selectivity of products was improved and **3a** was obtained more than ten times as much as **2a** (**2a**:**3a** = 9:91), even though the reaction proceeded slowly to afford the products in low yield (60%). A similar behavior has been observed in the reaction of **1b** with $CBrCl_3$. When the reaction was performed at room temperature, **2a** was mainly formed (**2a**:**3a** = 95:5). On the other hand, the reaction of **1b** at -23 °C or -78 °C gave **3a** almost exclusively (**2a**:**3a** = 5:95 or <2:>98). The decrease in the amount of **1b** (1.5 mmol per 1.0 mmol of $CBrCl_3$, Entry 9 in Table 2) did not influence the selectivity and yield of the products. However, the use of equimolar amounts of **1a** or **1b** (Entry 4 and 8) resulted in a decrease of the yields and selectivities.

The reaction of a ketene silyl acetal bearing alkyl group substituent (**1c**) with tetrahalomethanes afforded methyl 2-(trihalomethyl)octanoates (**3e-g**) as the major products, even at room temperature. Ketene silyl acetal **1d** reacted slowly with $CBrCl_3$ to give **3i** in poor yield because of its steric hindrance.

(2) Reaction of Ketene Silyl Acetals with Trihalomethanes. The treatment of ketene silyl acetal (**1a** or **1b**) with $CHBr_3$ provided a mixture of octyl (*E*)-3-bromoacrylate (**4b**) and octyl 3,3-dibromopropanoate (**5b**). Although trihalomethane, such as $CHXBr_2$ (X = Cl, F) or CHI_3, as well as $CHBr_3$, was applicable to this reaction,[7)] $CHCl_3$ did not react with **1a** or **1b**. In any case, except for the reaction of $CHFBr_2$ with **1a**, 3-haloacrylate **4** was a major product at room temperature. Meanwhile, the reaction of any trihalomethane at -23 °C gave **5** preferentially and improved the combined yields of adducts **4** and **5**. The radical addition of trihalomethane to ketene silyl acetal having an alkyl substituent **1c**

Table 3. Reaction of Ketene Silyl Acetal with Trihalomethane[a)]



Entry	Ketene silyl acetal	$CHXY_2$ X	Y	Reaction temp /°C	Reaction time /h	Product (Yield/%) $4^{b)c)}$		$5^{b)}$		$4^{c)d)}$	
1	**1a**	Cl	Br	r.t.	3	**4a**	(56)	**5a**	(13)		
2	**1a**	Cl	Br	-23	3	**4a**	(7)	**5a**	(86)	**4a**	(84)[e)]
3	**1a**	Br	Br	r.t.	3	**4b**	(59)	**5b**	(11)		
4	**1a**	Br	Br	-23	6	**4b**	(10)	**5b**	(79)	**4b**	(79)
5	**1a**	F	Br	r.t.	1.5	**4c**	(16)	**5c**	(36)		
6	**1a**	F	Br	-23	6	**4c**	(2)	**5c**	(87)	**4c**	(79)
7	**1a**	I	I	r.t.[f)]	3	**4d**	(37)	**5d**	(4)		
8	**1b**	Cl	Br	r.t.	3	**4a**	(60)	**5a**	(4)		
9	**1b**	Cl	Br	-23	3	**4a**	(10)	**5a**	(84)	**4a**	(88)[e)]
10	**1b**	Br	Br	r.t.	4	**4b**	(60)	**5b**	(9)		
11	**1b**	Br	Br	-23	6	**4b**	(13)	**5b**	(76)	**4b**	(82)
12	**1b**	F	Br	r.t.	1.5	**4c**	(22)	**5c**	(2)		
13	**1b**	F	Br	-23	6	**4c**	(3)	**5c**	(81)	**4c**	(82)
14	**1b**	I	I	r.t.[f)]	3	**4d**	(18)	**5d**	(24)		
15	**1c**	Cl	Br	r.t.	12	**4e**	(24)	**5e**	(54)[g)]	**4e**	(77)[e)]
16	**1c**	Br	Br	r.t.	12	**4f**	(5)	**5f**	(67)	**4f**	(67)
17	**1c**	F	Br	r.t.	12	**4g**	(2)	**5g**	(20)[g)]	**4g**	(21)

a) Ketene silyl acetal (2.0 mmol), trihalomethane $CHXY_2$ (1.0 mmol), and Et_3B (0.2 mmol) in hexane (5 ml) were employed. b) Yields based on trihalomethane were determined by the examination of ^{1}H-NMR of the mixture of **4** and **5** after purification. c) (*Z*)-isomer of **4a**, **4b**, or **4d** was isolated in less than 2% yield. (*Z*)-isomer of **4c**, **4e**, **4f**, or **4g** could not be detected. d) Treatment of crude product with Et_3N followed by purification afforded only **4**. e) **4a** or **4e** was obtained along with **4b** (5%) or **4f** (6%), respectively. f) At -23 °C, the reaction with CHI_3 is very slow. g) Diastereomeric mixture. **5e**; (50 : 50), **5g**; (55 : 45).

proceeded slowly and produced mainly **5**, even at room temperature.

3,3-Dihalopropanoates **5** were easily transformed into (*E*)-3-haloacrylates **4** by dehydrohalogenation with Et_3N. Thus, the addition of trihalomethane to **1a**, **1b**, or **1c** followed by treatment of the crude product with Et_3N afforded the corresponding **4**; the overall yields are shown in the last column of Table 3.

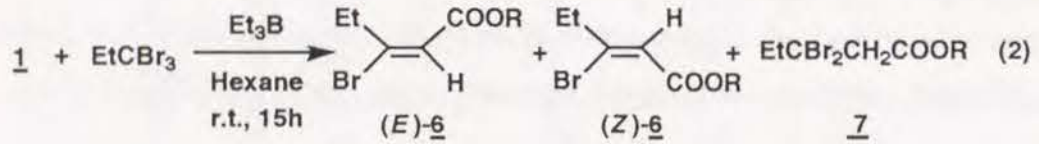
As shown in Table 4, AIBN also induced a radical addition of $CBrCl_3$ or $CHBr_3$ to ketene silyl acetal **1a** or **1b** to give **2a** or **4b** as a single product, respectively, without any contamination by **3a** or **5b**, though the yields were lower than those of a Et_3B-induced reaction, especially in the case of the $CHBr_3$ reaction.

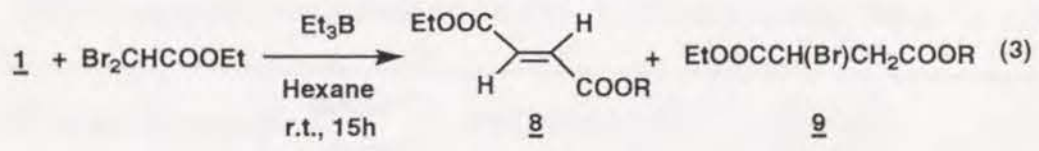
Table 4. AIBN Induced Reaction of Ketene Silyl Acetal with Polyhalomethane[a)]

Entry	Ketene Silyl Acetal	Polyhalomethane	Reaction time /h	Product (Yield /%)[b)]	
1	**1a**	$CBrCl_3$	1	**2a**	(85)
2	**1a**	$CHBr_3$	3	**4b**	(28)
3	**1b**	$CBrCl_3$	1	**2a**	(71)
4	**1b**	$CHBr_3$	3	**4b**	(18)

a) Ketene silyl acetal (2.0 mmol), polyhalomethane (1.0 mmol), and AIBN (0.1 mmol) were employed. All reactions were carried out at 80 °C in benzene. b) **3a** or **5b** could not be detected.

(3) Reaction of Ketene Silyl Acetals with 1,1,1-Tribromopropane or Ethyl Dibromoacetate. The use of 1,1,1-tribromopropane[8] or ethyl dibromoacetate in place of polyhalomethanes resulted in the formation of the corresponding 3-bromo-2-pentenoate (**6**) or fumarate (**8**) as a major product (eq 2, 3). These polyhalo compounds were less reactive than polyhalomethanes and the yields of products were somewhat poor.

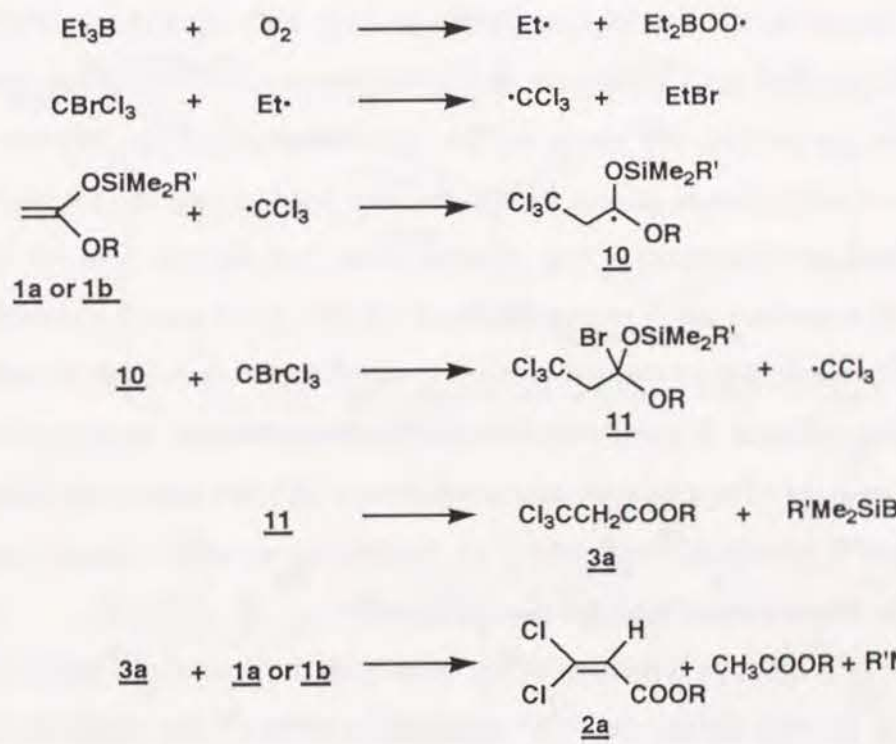




(4) Mechanism. In the presence of a radical scavenger, such as galvinoxyl,[9] Et_3B did not initiate the reaction of ketene silyl acetal **1a** with $CBrCl_3$. In addition, AIBN, as well as Et_3B, induced a reaction at 80 °C. These results support the idea that the Et_3B-induced reaction includes a radical chain mechanism. Moreover, the formation of octyl acetate and *t*-$BuMe_2SiX$ (X = Br, Cl) was observed in addition to **2a** and **3a** in the reaction of **1a** and $CBrCl_3$. Thus, we were tempted to assume the following reaction mechanism for the formation of **2a** or **3a** (Scheme 1): (1) Ethyl radical, generated by the action of molecular oxygen on Et_3B,[10] abstracts bromine from $CBrCl_3$ to give $\cdot CCl_3$; (2) the addition of $\cdot CCl_3$

to ketene silyl acetal (**1**) provides a new radical intermediate (**10**) which is a carbon radical bearing OR and $OSiMe_2R'$ groups;[2a] (3) intermediate **10** abstracts bromine from $CBrCl_3$ to afford an unstable bromide (**11**) and regenerates $\cdot CCl_3$; (4) elimination of silyl bromide leads **11** to 3,3,3-trichloropropanoates (**3a**); and (5) dehydrohalogenation of **3a** with excess **1** gives 3,3-dichloroacrylate (**2a**).

Scheme 1.



However, the last dehydrochlorination step (5) was denied in the following experiments. A mixture of $CBrCl_3$ and **1a** or **1b** was stirred for 1 h at -23 °C. Injection of a part of the reaction mixture to gas chromatography (GLPC) revealed that **3a** was formed as a major product (**2a**:**3a** = 4:6 or 5:95). The reaction mixture was warmed to room temperature and stirred for another 1 h. A second injection of

the reaction mixture to GLPC showed that the ratio of **2a** to **3a** did not change, in spite of the presence of excess **1a** or **1b**. A similar result could be found in the reaction of $CHBr_3$ with **1b**. Moreover, treatment of **3a** with ketene silyl acetal **1b** in hexane resulted in a complete recovery of **3a**. The addition of TMSBr to a reaction mixture of **3a** and **1b** also did not promote the formation of **2a**. These facts would suggest that **2a** is produced directly from the same intermediate **11** independently of the formation of **3a**.

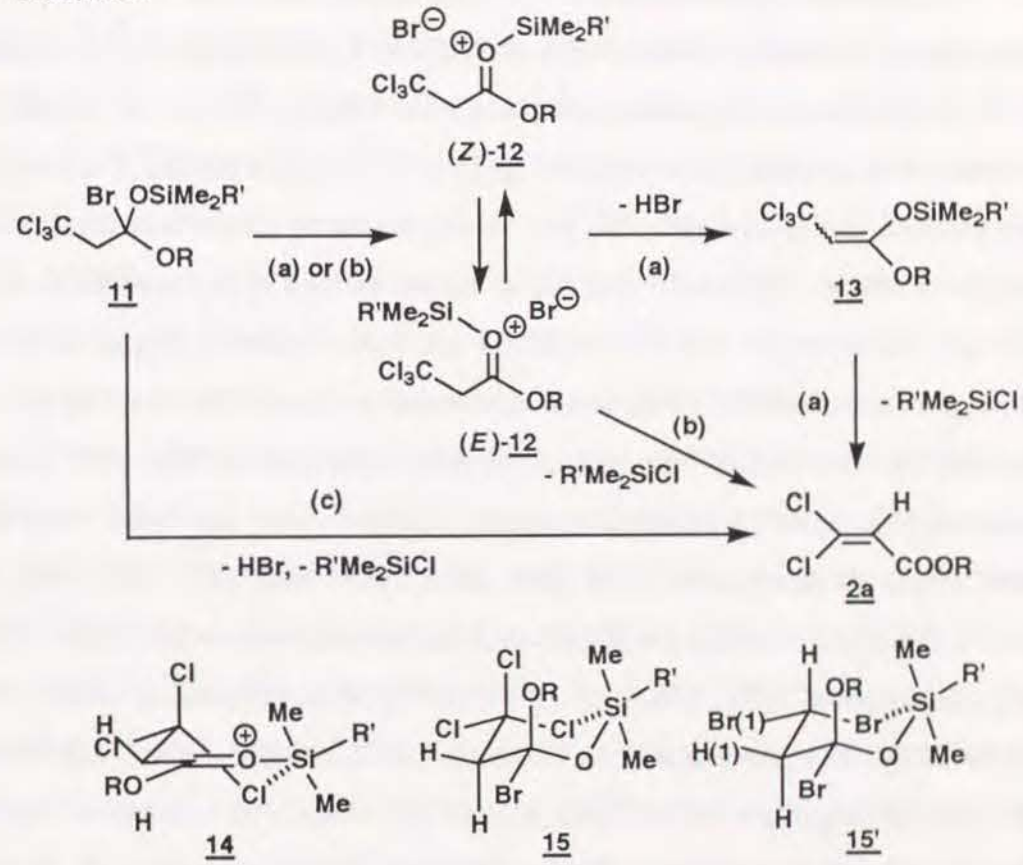
The conceivable routes for the formation of **2a** from **11** are described in Scheme 2, though the mechanism is not clear at present. Path (**a**) or (**b**) involves an oxonium intermediate (**12**), which is derived from bromides **11** by the elimination of the Br^- anion. In path (**a**), deprotonation from **12** by ketene silyl acetal, followed by elimination of silyl chloride, affords **2a**. On the other hand, in path (**b**) the reaction proceeds through a 6-membered ring transition state (**14**) derived from the *trans* isomer of **12** to produce **2a**. The elimination of the silyl group and Cl is attributed to the high Lewis acidity of the silyl group. However, since it is difficult to assume the formation of such a polar intermediate as **12** in hexane, we propose an alternative path (**c**). The concerted anti elimination of HCl and $R'Me_2SiBr$ through a chair type 6-membered transition state possessing an axial alkoxyl group stabilized by an anomeric effect (**15**) gave **2a** directly.

The (*E*)-selective formation of the product in the reaction of ketene silyl acetal **1a** or **1b** with $CHBr_3$ could be explained in terms of the transition state model **15'**. In **15'**, bromine (1) occupies the equatorial position because of the steric repulsion of RO or the substituent on silicon. The attack of ketene silyl acetal on equatorial hydrogen (1) causes a double anti elimination of HBr and $R'Me_2SiBr$ to afford (*E*)-octyl 3-bromoacrylate (**4b**).

The temperature dependence of the distribution of products **2a** and **3a** could be explained as follows. The formation of **2a** includes the dehydrohalogenation of

11 or **12** by a second equivalent of ketene silyl acetal, which is favorable at room temperature. In contrast, this intermolecular reaction is slower than the elimination of $R'Me_2SiBr$ from **11** at low temperature, such as -78 °C, and **3a** becomes a major product.

Scheme 2.



Experimental

Preparation of Ketene Silyl Acetal. Ketene silyl acetals **1a-d** were prepared according to the reported procedure.[11] The physical data for **1a-d** are described in the literature.[2a]

Reaction of Ketene Silyl Acetal with Polyhalomethane. Typical procedure is as follows. Under argon atmosphere, Et_3B (0.96 M hexane solution, 0.21 ml, 0.20 mmol) was added to a solution of $CBrCl_3$ (0.20 g, 1.0 mmol) and ketene *t*-butyldimethylsilyl octyl acetal (0.57 g, 2.0 mmol) in hexane (5 ml) at room temperature. After stirring for 30 min, sat. aq $NaHCO_3$ (5 ml) was added to the reaction mixture. The mixture was stirred vigorously for 1 h, then poured into water (20 ml), and extracted with hexane (20 ml x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residual oil was purified by silica-gel column chromatography using hexane-ether (40 : 1) as an eluent to give octyl 3, 3-dichloroacrylate (**2a**) in 93% yield: Bp 78–83 °C (1 Torr, bath temp); IR (neat) 2954, 2924, 2854, 1735, 1605, 1466, 1297, 1171, 963, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.59–1.73 (m, 2H), 4.16 (t, *J*=6.7 Hz, 2H), 6.38 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.00, 22.58, 25.83, 28.44, 29.11 (two peaks), 31.71, 65.16, 120.05, 137.28, 162.31; MS (70 eV) *m/z* (rel intensity) 219 (M^++2-^{35}Cl, 6), 217 (M^+-^{35}Cl, 16), 143 (M^++2-C_8H_{15}, 39), 141 (M^+-C_8H_{15}, 62), 112 (62), 111 (27), 84 (78), 83 (71), 70 (100), 69 (55), 56 (58). Found: C, 52.35; H, 7.36%. Calcd for $C_{11}H_{18}Cl_2O_2$: C, 52.19; H, 7.17%.

Octyl 3, 3, 3-Trichloropropanoate (3a): Bp 102–107 °C (1 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1749, 1467, 1346, 1284, 1180, 977, 715, 686 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.60–1.75 (m, 2H), 3.74 (s, 2H), 4.20 (t, *J*=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.06, 22.61, 25.81, 28.41, 29.10 (two peaks), 31.74, 57.85, 65.83, 92.72, 165.31; MS (70 eV)

m/z (rel intensity) 179 (M^++2-C_8H_{15}, 9), 177 (M^+-C_8H_{15}, 9), 143 (17), 141 (29), 112 (60), 111 (16), 84 (100), 83 (71), 70 (87), 56 (61). Found: C, 45.77; H, 6.65%. Calcd for $C_{11}H_{19}Cl_3O_2$: C, 45.62; H, 6.61%.

Octyl 3, 3-Dibromoacrylate (2b): Bp 114–118 °C (2 Torr, bath temp); IR (neat) 2952, 2924, 2852, 1733, 1594, 1297, 1168 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.59–1.72 (m, 2H), 4.16 (t, *J*=6.7 Hz, 2H), 7.01 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.62, 25.88, 28.46, 29.14 (two peaks), 31.74, 65.32, 106.35, 128.09, 163.14; MS (70 eV) *m/z* (rel intensity) 263 (M^++2-^{79}Br, 3), 261 (M^+-^{79}Br, 3), 233 (M^++4-C_8H_{15}, 24), 231 (M^++2-C_8H_{15}, 51), 229 (M^+-C_8H_{15}, 24), 215 (38), 213 (81), 211 (42), 112 (26), 84 (58), 83 (48), 70 (84), 69 (62), 56 (82), 55 (78), 43 (90), 42 (46), 41 (100). Found: C, 38.86; H, 5.55%. Calcd for $C_{11}H_{18}Br_2O_2$: C, 38.62; H, 5.30%.

Octyl 3, 3-Difluoroacrylate (2c): Bp 69–73 °C (9 Torr, bath temp); IR (neat) 2954, 2926, 2856, 1749, 1734, 1711, 1357, 1279, 1137 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.58–1.72 (m, 2H), 4.15 (t, *J*=6.7 Hz, 2H), 4.98 (dd, *J*=21.8, 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.58, 25.80, 28.47, 29.12 (two peaks), 31.72, 64.98, 77.10 (dd, *J*=28.6, 9.1 Hz), 161.87 (dd, *J*=311.7, 298.5 Hz), 162.97 (dd, *J*=17.1, 7.5 Hz); ^{19}F NMR ($CDCl_3$) δ -64.74 (dd, *J*=21.7, 15.8 Hz, 1F), -70.85 (dd, *J*=15.8, 2.0 Hz, 1F); MS (70 eV) *m/z* (rel intensity) 112 (7), 109 (M^+-C_8H_{15}, 26), 91 (M^+-C_8H_{15}-H_2O, 100), 43 (52), 41 (51). Found: C, 60.12; H, 8.47%. Calcd for $C_{11}H_{18}F_2O_2$: C, 59.98; H, 8.24%.

Octyl 3-Bromo-3, 3-difluoropropanoate (3c): Bp 67–71 °C (1 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1750, 1356, 1285, 1218, 1176, 1092, 1024 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.58–1.72 (m, 2H), 3.45 (t, *J*=13.2 Hz, 2H), 4.18 (t, *J*=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.06, 22.61, 25.74, 28.36, 29.09 (two peaks), 31.73, 49.11 (t, *J*=23.5 Hz), 66.00, 116.36

(t, J=305.9 Hz), 164.48 (t, J=4.5 Hz); ^{19}F NMR ($CDCl_3$) δ -44.15 (t, J=13.3 Hz); MS (70 eV) m/z (rel intensity) 191 (M^++2-C_8H_{15}, 3), 189 (M^+-C_8H_{15}, 3), 173 (M^++2-C_8H_{15}-H_2O, 11), 171 (M^+-C_8H_{15}-H_2O, 14), 145 (12), 143 (13), 112 (11), 84 (63), 71 (50), 70 (82), 69 (60), 57 (76), 56 (91), 55 (80), 43 (91), 42 (60), 41 (100). Found: C, 44.02; H, 6.42%. Calcd for $C_{11}H_{19}BrF_2O_2$: C, 43.87; H, 6.36%.

Octyl 3, 3-Diiodoacrylate (2d): Bp 139–143 °C (0.31 Torr, bath temp); IR (neat) 2950, 2922, 2852, 1727, 1570, 1291, 1252, 1168, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=6.5 Hz, 3H), 1.28 (bs, 10H), 1.60–1.72 (m, 2H), 4.14 (t, J=6.7 Hz, 2H), 7.80 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.58, 25.85, 28.43, 29.10 (two peaks), 31.70, 65.14, 140.43, 164.51 (Another olefinic ^{13}C could not be detected.); MS (70 eV) m/z (rel intensity) 436 (M^+, 4), 325 (M^+-C_8H_{15}, 44), 324 (100), 307 (61), 279 (14), 197 (12), 152 (28), 127 (12), 43 (80), 41 (63). Found: C, 30.57; H, 4.20%. Calcd for $C_{11}H_{18}I_2O_2$: C, 30.30; H, 4.16%.

Methyl 2-(Trichloromethyl)octanoate (3e): Bp 92–97 °C (3 Torr, bath temp); IR (neat) 2954, 2924, 2856, 1752, 1458, 1436, 1349, 1257, 1202, 1165, 779, 722, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=6.5 Hz, 3H), 1.20–1.45 (m, 8H), 1.91-2.19 (m, 2H), 3.48 (dd, J=10.2, 4.0 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 13.92, 22.43, 26.88, 28.72, 30.23, 31.39, 52.23, 65.58, 98.17, 169.33; MS (70 eV) m/z (rel intensity) 241 (M^++2-^{35}Cl, 5), 239 (M^+-^{35}Cl, 8), 159 (M^++4-^{35}Cl-C_6H_{12}, 10), 157 (M^++2-^{35}Cl-C_6H_{12}, 68), 155 (M^+-^{35}Cl-C_6H_{12}, 100), 116 (18), 109 (10), 107 (10). Found: C, 43.72; H, 6.32%. Calcd for $C_{10}H_{17}Cl_3O_2$: C, 43.58; H, 6.22%.

Methyl 3, 3-Dibromo-2-hexylacrylate (2f): Bp 74–78 °C (1 Torr, bath temp); IR (neat) 2952, 2926, 2856, 1733, 1457, 1434, 1278, 1247, 1194, 1136, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=6.4 Hz, 3H), 1.25–1.60 (m, 8H), 2.40–2.48 (m, 2H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 14.01, 22.47, 26.97, 28.64, 31.39,

35.75, 52.53, 93.54, 140.99, 167.20; MS (70 eV) m/z (rel intensity) 260 (M^++4-C_5H_{10}, 8), 258 (M^++2-C_5H_{10}, 17), 256 (M^+-C_5H_{10}, 9), 249 (M^++2-^{79}Br, 34), 247 (M^+-^{79}Br, 39), 245 (25), 179 (25), 177 (26), 135 (21), 107 (75), 43 (100), 41 (54). Found: C, 36.88; H, 5.07%. Calcd for $C_{10}H_{16}Br_2O_2$: C, 36.61; H, 4.92%.

Methyl 2-(Tribromomethyl)octanoate (3f): Bp 88–93 °C (2 Torr, bath temp); IR (neat) 2952, 2926, 2856, 1746, 1457, 1434, 1343, 1255, 1200, 1164, 701, 627 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J=6.5 Hz, 3H), 1.20–1.50 (m, 8H), 1.93–2.25 (m, 2H), 3.56 (dd, J=10.1, 3.8 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 14.00, 22.48, 26.78, 28.78, 31.44, 32.94, 39.11, 52.22, 67.79, 170.09; MS (70 eV) m/z (rel intensity) 331 (M^++4-^{79}Br, 2), 329 (M^++2-^{79}Br, 4), 327 (M^+-^{79}Br, 3), 247 (M^++4-^{79}Br-C_6H_{12}, 6), 245 (M^++2-^{79}Br-C_6H_{12}, 12), 243 (M^+-^{79}Br-C_6H_{12}, 6), 169 (22), 109 (31), 107 (39), 59 (62), 43 (100), 41 (94), 39 (57). Found: C, 29.61; H, 4.17%. Calcd for $C_{10}H_{17}Br_3O_2$: C, 29.37; H, 4.19%.

Methyl 3, 3-Difluoro-2-hexylacrylate (2g): Bp 90–95 °C (35 Torr, bath temp); IR (neat) 2956, 2928, 2858, 1749, 1716, 1440, 1347, 1195, 1157, 1129, 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=6.4 Hz, 3H), 1.25–1.53 (m, 8H), 2.18–2.27 (m, 2H), 3.79 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 13.95, 22.52, 24.46, 28.50, 28.65, 31.45, 51.95, 88.74 (dd, J=24.4, 3.7 Hz), 159.78 (dd, J=309.8, 294.5 Hz), 165.53 (dd, J=12.2, 5.4 Hz); ^{19}F NMR ($CDCl_3$) δ -70.23 (s, 1F), -75.05 (s, 1F); MS (70 eV) m/z (rel intensity) 186 (M^+-HF, 4), 175 (M^+-OMe, 17), 144 (34), 143 (61), 127 (20), 107 (24), 105 (34), 101 (43), 43 (100), 41 (55). Found: C, 58.19; H, 8.07%. Calcd for $C_{10}H_{16}F_2O_2$: C, 58.24; H, 7.82%.

Methyl 2-(Bromodifluoromethyl)octanoate (3g): Bp 76–80 °C (7 Torr, bath temp); IR (neat) 2954, 2926, 2858, 1752, 1459, 1437, 1347, 1259, 1198, 1170, 1096, 951, 933 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=6.3 Hz, 3H), 1.30 (bs, 8H), 1.73–2.06 (m, 2H), 3.27 (td, J=10.8, 4.3 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 13.91, 22.44, 26.69, 27.76, 28.72, 31.35, 52.50, 58.54 (t, J=20.9 Hz), 120.44 (t,

J=309.2 Hz), 168.35 (t, J=3.9 Hz); ^{19}F NMR ($CDCl_3$) δ -47.63 (dd, J=158.0, 10.8 Hz, 1F), -48.33 (dd, J=158.0, 10.8 Hz, 1F); MS (70 eV) m/z (rel intensity) 257 (M^++2-OMe, 1), 255 (M^+-OMe, 1), 207 (M^+-^{79}Br, 21), 127 (10), 123 (100), 107 (11), 43 (56), 41 (51). Found: C, 41.94; H, 6.04%. Calcd for $C_{10}H_{17}BrF_2O_2$: C, 41.83; H, 5.97%.

Hexyl 3, 3, 3-Trichloro-2, 2-dimethylpropanoate (3i): Bp 88–93 °C (1 Torr, bath temp); IR (neat) 2954, 2930, 2858, 1737, 1469, 1257, 1155, 901, 795, 743, 638 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=6.5 Hz, 3H), 1.25–1.46 (m, 6H), 1.60–1.76 (m, 8H, including 1.64 (s, 6H)), 4.17 (t, J=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.89, 22.43, 23.24, 25.52, 28.28, 31.24, 59.92, 65.95, 104.83, 170.62; MS (12 eV) m/z (rel intensity) 211 (M^++6-C_6H_{11}, 0.4), 209 (M^++4-C_6H_{11}, 5), 207 (M^++2-C_6H_{11}, 15), 205 (M^+-C_6H_{11}, 14), 171 (15), 169 (22), 133 (11), 126 (38), 124 (56), 85 (60), 84 (100), 43 (73). Found: C, 45.69; H, 6.70%. Calcd for $C_{11}H_{19}Cl_3O_2$: C, 45.62; H, 6.61%.

Stereochemistry of 3-Haloacrylate Derivatives. Stereochemistry of octyl (E)-3-haloacrylates **4a-d** was determined by the examination of the ^{1}H NMR chemical shifts and coupling constants of olefinic protons. The assignment of methyl (E)-3-halo-2-hexylacrylates **4e-g** was also based on inspection of chemical shift of olefinic proton. The δ values of olefinic proton of **4e-g** are similar to that of proton on 3-position of the respective octyl (E)-3-haloacrylate **4a-c**. In addition, the comparison of the ^{1}H NMR spectra of **4f** with methyl (E) or (Z)-3-bromo-2-methylacrylate[12] supported that **4f** had (E)-stereochemistry. Methyl (E)-3-bromo-2-methylacrylate ($CDCl_3$): δ 2.01 (d, J=1.7 Hz, 3H), 3.77 (s, 3H), 7.54 (q, J=1.7 Hz, 1H). (Z)-isomer (minor product) ($CDCl_3$): δ 2.00 (d, J=1.6 Hz, 3H), 3.82 (s, 3H), 6.57 (q, J=1.6 Hz, 1H). Methyl (E)-3-bromo-2-hexylacrylate (**4f**) ($CDCl_3$): δ 0.89 (t, J=6.5 Hz, 3H), 1.25–1.55 (m, 8H), 2.43–2.51 (m, 2H), 3.76 (s, 3H), 7.51 (s, 1H).

Octyl (E)-3-Chloroacrylate (4a): Bp 69–74 °C (1 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1726, 1612, 1296, 1254, 1161 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=6.3 Hz, 3H), 1.28 (bs, 10H), 1.59–1.72 (m, 2H), 4.15 (t, J=6.7 Hz, 2H), 6.25 (d, J=13.4 Hz, 1H), 7.37 (d, J=13.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.03, 22.59, 25.85, 28.52, 29.14 (two peaks), 31.73, 65.05, 124.90, 137.32, 164.10; MS (70 eV) m/z (rel intensity) 183 (M^+-^{35}Cl, 3), 112 (18), 109 (M^++2-C_8H_{15}, 10), 107 (M^+-C_8H_{15}, 25), 91 (M^++2-C_8H_{15}-H_2O, 37), 89 (M^+-C_8H_{15}-H_2O, 100), 70 (66), 69 (52), 56 (69), 55 (62), 43 (52), 41 (63). Found: C, 60.22; H, 8.75%. Calcd for $C_{11}H_{19}ClO_2$: C, 60.41; H, 8.76%.

Octyl (Z)-3-Chloroacrylate: Bp 71–75 °C (0.80 Torr, bath temp); IR (neat) 2952, 2924, 2854, 1732, 1619, 1467, 1349, 1278, 1223, 1168, 809 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J=6.4 Hz, 3H), 1.28 (bs, 10H), 1.58–1.78 (m, 2H), 4.18 (t, J=6.7 Hz, 2H), 6.20 (d, J=8.3 Hz, 1H), 6.70 (d, J=8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.06, 22.63, 25.91, 28.54, 29.16 (two peaks), 31.76, 64.89, 121.56, 132.17, 163.57; MS (70 eV) m/z (rel intensity) 183 (M^+-^{35}Cl, 0.8), 112 (11), 109 (M^++2-C_8H_{15}, 12), 107 (M^+-C_8H_{15}, 34), 91 (M^++2-C_8H_{15}-H_2O, 26), 89 (M^+-C_8H_{15}-H_2O, 92), 70 (50), 56 (61), 55 (62), 43 (79), 41 (100). Found: C, 60.53; H, 8.95%. Calcd for $C_{11}H_{19}ClO_2$: C, 60.41; H, 8.76%.

Octyl 3-Bromo-3-chloropropanoate (5a): Bp 86–91 °C (1 Torr, bath temp); IR (neat) 2954, 2924, 2854, 1741, 1467, 1350, 1276, 1228, 1183, 1148, 685, 622 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=6.5 Hz, 3H), 1.28 (bs, 10H), 1.56–1.71 (m, 2H), 3.39 (d, J=6.8 Hz, 2H), 4.15 (t, J=6.7Hz, 2H), 6.07 (t, J=6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.05, 22.59, 25.77, 28.42, 29.10 (two peaks), 31.71, 49.52, 52.87, 65.60, 167.80; MS (70 eV) m/z (rel intensity) 191 (M^++4-C_8H_{15}, 0.9), 189 (M^++2-C_8H_{15}, 4.2), 187 (M^+-C_8H_{15}, 3.3), 173 (M^++4-C_8H_{15}-H_2O, 1.3), 171 (M^++2-C_8H_{15}-H_2O, 5.5), 169 (M^+-C_8H_{15}-H_2O, 3.6), 143 (9), 112 (9), 70 (61), 56 (88), 55 (67), 43 (87), 42 (54), 41 (100). Found: C, 44.29; H, 6.83%.

Calcd for $C_{11}H_{20}BrClO_2$: C, 44.09; H, 6.73%.

Octyl (*E*)-3-Bromoacrylate (4b): Bp 86–91 °C (2 Torr, bath temp); IR (neat) 2952, 2926, 2854, 1725, 1607, 1297, 1262, 1229, 1153 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.59–1.72 (m, 2H), 4.15 (t, *J*=6.7 Hz, 2H), 6.53 (d, *J*=13.9 Hz, 1H), 7.60 (d, *J*=13.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.03, 22.59, 25.85, 28.52, 29.13 (two peaks), 31.72, 65.12, 126.38, 128.87, 164.10; MS (70 eV) *m/z* (rel intensity) 183 (M^+-^{79}Br, 5), 153 (M^++2-C_8H_{15}, 27), 151 (M^+-C_8H_{15}, 28), 135 (M^++2-C_8H_{15}-H_2O, 90), 133 (M^+-C_8H_{15}-H_2O, 94), 112 (31), 107 (22), 105 (22), 84 (59), 83 (58), 70 (100), 69 (70), 56 (94), 55 (86), 43 (81), 42 (56), 41 (96). Found: C, 50.28; H, 7.56%. Calcd for $C_{11}H_{19}BrO_2$: C, 50.20; H, 7.28%.

Octyl (*Z*)-3-Bromoacrylate: Bp 65–70 °C (0.43 Torr, bath temp); IR (neat) 2952, 2924, 2852, 1732, 1614, 1467, 1333, 1208, 1166, 808 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.60–1.75 (m, 2H), 4.18 (t, *J*=6.7 Hz, 2H), 6.63 (d, *J*=8.3 Hz, 1H), 6.99 (d, *J*=8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.03, 22.59, 25.89, 28.49, 29.12 (two peaks), 31.72, 64.93, 120.89, 124.59, 163.99; MS (70 eV) *m/z* (rel intensity) 183 (M^+-^{79}Br, 3), 153 (M^++2-C_8H_{15}, 55), 151 (M^+-C_8H_{15}, 59), 135 (M^++2-C_8H_{15}-H_2O, 87), 133 (M^+-C_8H_{15}-H_2O, 87), 112 (34), 107 (18), 105 (21), 84 (53), 70 (84), 69 (62), 56 (83), 55 (76), 43 (75), 42 (51), 41 (100). Found: C, 50.26; H, 7.32%. Calcd for $C_{11}H_{19}BrO_2$: C, 50.20; H, 7.28%.

Octyl 3, 3-Dibromopropanoate (5b): Bp 89–94 °C (1 Torr, bath temp); IR (neat) 2954, 2924, 2852, 1740, 1348, 1276, 1257, 1225, 1147, 637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.60–1.75 (m, 2H), 3.52 (d, *J*=7.0 Hz, 2H), 4.15 (t, *J*=6.7 Hz, 2H), 5.95 (t, *J*=7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.62, 25.81, 28.46, 29.12 (two peaks), 31.74, 36.24, 50.37, 65.66, 168.16; MS (70 eV) *m/z* (rel intensity) 235 (M^++4-C_8H_{15}, 10), 233

(M^++2-C_8H_{15}, 17), 231 (M^+-C_8H_{15}, 9), 217 (M^++4-C_8H_{15}-H_2O, 8), 215 (M^++2-C_8H_{15}-H_2O, 14), 213 (M^+-C_8H_{15}-H_2O, 6), 189 (10), 187 (21), 185 (12), 135 (18), 133 (20), 112 (35), 84 (78), 83 (67), 70 (92), 69 (63), 57 (67), 56 (87), 55 (85), 43 (97), 42 (60), 41 (100). Found: C, 38.51; H, 5.86%. Calcd for $C_{11}H_{20}Br_2O_2$: C, 38.40; H, 5.86%.

Octyl (*E*)-3-Fluoroacrylate (4c): Bp 74–78 °C (7 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1730, 1662, 1306, 1273, 1133, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.58–1.73 (m, 2H), 4.14 (t, *J*=6.7 Hz, 2H), 5.78 (dd, *J*=14.9, 11.3 Hz, 1H), 7.56 (dd, *J*=79.9, 11.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.05, 22.61, 25.87, 28.54, 29.16 (two peaks), 31.75, 64.83, 106.79 (d, *J*=14.9 Hz), 162.91 (d, *J*=279.8 Hz), 165.33 (d, *J*=22.9 Hz); ^{19}F NMR ($CDCl_3$) δ -112.22 (dd, *J*=79.7, 14.8 Hz); MS (70 eV) *m/z* (rel intensity) 112 (7), 91 (M^+-C_8H_{15}, 19), 73 (M^+-C_8H_{15}-H_2O, 100). Found: C, 65.26; H, 9.64%. Calcd for $C_{11}H_{19}FO_2$: C, 65.32; H, 9.47%.

Octyl 3-Bromo-3-fluoropropanoate (5c): Bp 74–78 °C (1 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1740, 1328, 1307, 1265, 1231, 1158, 1034, 638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.58–1.75 (m, 2H), 3.22 (ddd, *J*=23.8, 16.5, 5.1 Hz, 1H), 3.39 (ddd, *J*=16.5, 12.1, 7.0 Hz, 1H), 4.15 (t, *J*=6.7 Hz, 2H), 6.77 (ddd, *J*=49.5, 7.0, 5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.06, 22.61, 25.77, 28.42, 29.12 (two peaks), 31.73, 45.91 (d, *J*=22.8 Hz), 65.65, 88.98 (d, *J*=252.1 Hz), 167.41 (d, *J*=6.9 Hz); ^{19}F NMR ($CDCl_3$) δ -134.67 (ddd, *J*=49.2, 21.7, 13.8 Hz); MS (70 eV) *m/z* (rel intensity) 173 (M^++2-C_8H_{15}, 3), 171 (M^+-C_8H_{15}, 3), 155 (M^++2-C_8H_{15}-H_2O, 6), 153 (M^+-C_8H_{15}-H_2O, 8), 127 (8), 125 (10), 112 (8), 70 (61), 56(83), 55 (67), 43 (100), 42 (54), 41 (96). Found: C, 46.95; H, 7.10%. Calcd for $C_{11}H_{20}BrFO_2$: C, 46.66; H, 7.12%.

Octyl (*E*)-3-Iodoacrylate (4d): Bp 89–93 °C (1 Torr, bath temp); IR (neat) 2952, 2924, 2852, 1723, 1592, 1296, 1258, 1214, 1145 cm^{-1}; ^1H NMR

($CDCl_3$) 0.89 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.59–1.72 (m, 2H), 4.14 (t, *J*=6.7 Hz, 2H), 6.89 (d, *J*=14.8 Hz, 1H), 7.87 (d, *J*=14.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.05, 22.59, 25.85, 28.51, 29.12 (two peaks), 31.73, 65.12, 99.17, 136.54, 164.20; MS (70 eV) *m/z* (rel intensity) 199 (M^+-C_8H_{15}, 47), 181 (M^+-C_8H_{15}-H_2O, 100), 153 (29), 127 (12), 112 (25), 70 (55), 56 (54), 55 (52), 43 (55), 41 (61). Found: C, 42.72; H, 6.39%. Calcd for $C_{11}H_{19}IO_2$: C, 42.60; H, 6.17%.

Octyl (Z)-3-Iodoacrylate: Bp 75–80 °C (0.73 Torr, bath temp); IR (neat) 2952, 2922, 2852, 1729, 1600, 1323, 1195, 1164 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.62-1.76 (m, 2H), 4.19 (t, *J*=6.7 Hz, 2H), 6.91 (d, *J*=8.9 Hz, 1H), 7.45 (d, *J*=8.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.63, 25.94, 28.53, 29.16 (two peaks), 31.76, 65.01, 94.43, 129.99, 164.68; MS (70 eV) *m/z* (rel intensity) 310 (M^+, 2), 199 (M^+-C_8H_{15}, 67), 198 (92), 181 (M^+-C_8H_{15}-H_2O, 100), 153 (25), 112 (18), 56 (50), 43 (60), 41 (67). Found: C, 42.52; H, 6.17%. Calcd for $C_{11}H_{19}IO_2$: C, 42.60; H, 6.17%.

Octyl 3, 3-Diiodopropanoate (5d): Bp 105–109 °C (0.82 Torr, bath temp); IR (neat) 2950, 2922, 2852, 1737, 1342, 1269, 1209, 1134, 1084 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.60–1.73 (m, 2H), 3.72 (d, *J*=7.4 Hz, 2H), 4.14 (t, *J*=6.6 Hz, 2H), 5,27 (t, *J*=7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -43.32, 14.07, 22.61, 25.87, 28.50, 29.12 (two peaks), 31.74, 53.44, 65.56, 169.47; MS (70 eV) *m/z* (rel intensity) 438 (M^+, 2), 311 (M^+-I, 4), 281 (10), 199 (11), 181 (16), 154 (13), 113 (22), 71 (78), 57 (100), 43 (80). Found: C, 30.39; H, 4.56%. Calcd for $C_{11}H_{20}I_2O_2$: C, 30.16; H, 4.60%.

Methyl (*E*)-3-Chloro-2-hexylacrylate (4e): Bp 62–66 °C (6 Torr, bath temp); IR (neat) 2954, 2926, 2856, 1725, 1608, 1459, 1437, 1338, 1322, 1244, 1196, 1133, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (d, *J*=6.4 Hz, 3H), 1.20–1.55 (m, 8H), 2.41–2.49 (m, 2H), 3.77 (s, 3H), 7.29 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.55, 27.28, 27.75, 29.05, 31.54, 52.05, 131.92, 135.52, 165.83; MS (70 eV) *m/z*

(rel intensity) 175 (M^++2-OMe, 2), 173 (M^+-OMe, 7), 170 (6), 169 (M^+-^{35}Cl, 49), 136 (M^++2-C_5H_{10}, 10), 134 (M^+-C_5H_{10}, 31), 125 (14), 121 (11), 109 (52), 103 (20), 43 (100), 41 (51). Found: C, 58.47; H, 8.35%. Calcd for $C_{10}H_{17}ClO_2$: C, 58.68; H, 8.37%.

Methy 2-(Bromochloromethyl)octanoate (5e, diastereomeric mixture (50:50)): Bp 78–83 °C (5 Torr, bath temp); IR (neat) 2952, 2924, 2856, 1741, 1459, 1437, 1356, 1257, 1203, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1,28 (bs, 8H), 1.65 –2.02 (m, 2H), 3.07 (ddd, *J*=9.8, 8.2, 4.0 Hz, 0.50H), 3.12 (ddd, *J*=10.0, 8.2, 4.0 Hz, 0.50H), 3.76 (s, 3H), 5.88 (d, *J*=8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.01, 22.50, 26.83, 28.89, 30.23, 30.58, 31.46, 52.25, 57.55, 57.78, 59.13, 59.75, 171.19, 171.47; MS (70 eV) *m/z* (rel intensity) 257 (M^++4-OMe, 1.3), 255 (M^++2-OMe, 5.3), 253 (M^+-OMe, 3.8), 207 (M^++2-^{79}Br, 25), 205 (M^+-^{79}Br, 73), 173 (23), 157 (20), 123 (80), 122 (18), 121 (100), 109 (76), 59 (75), 55 (73), 43 (76), 41 (74), 39 (52). Found: C, 42.35; H, 6.61%. Calcd for $C_{10}H_{18}BrClO_2$: C, 42.05; H, 6.35%.

Methyl (*E*)-3-Bromo-2-hexylacrylate (4f): Bp 70–74 °C (5 Torr, bath temp); IR (neat) 2954, 2926, 2856, 1724, 1608, 1436, 1293, 1232, 1129 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.25–1.55 (m, 8H), 2.43–2.51 (m, 2H), 3.76 (s, 3H), 7.51 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.03, 22.53, 27.62, 29.03, 29.68, 31.51, 52.11, 122.55, 138.30, 165.29; MS (70 eV) *m/z* (rel intensity) 219 (M^++2-OMe, 4.1), 217 (M^+-OMe, 3.5), 180 (M^++2-C_5H_{10}, 15), 178 (M^+-C_5H_{10}, 16), 170 (11), 169 (M^+-^{79}Br, 100), 137 (16), 109 (58), 43 (81). Found: C, 48.14; H, 7.06%. Calcd for $C_{10}H_{17}BrO_2$: C, 48.21; H, 6.88%.

Methyl 2-(Dibromomethyl)octanoate (5f): Bp 76–80 °C (1 Torr, bath temp); IR (neat) 2952, 2924, 2854, 1740, 1458, 1435, 1353, 1255, 1212, 1158, 662, 615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1.29 (bs, 8H), 1.64–2.03 (m, 2H), 3.14 (ddd, *J*=10.0, 8.3, 3.9 Hz, 1H), 3.76 (s, 3H), 5.80 (d, *J*=8.2 Hz, 1H);

^{13}C NMR ($CDCl_3$) δ 14.00, 22.49, 26.85, 28.87, 31.29, 31.45, 44.26, 52.25, 57.86, 171.32; MS (70 eV) *m/z* (rel intensity) 301 (M^++4-OMe, 0.7), 299 (M^++2-OMe, 1.3), 297 (M^+-OMe, 0.7), 251 (M^++2-^{79}Br, 20), 249 (M^+-^{79}Br, 20), 167 (92), 165 (100), 135 (11), 133 (11), 109 (38), 41 (53). Found: C, 36.69; H, 5.76%. Calcd for $C_{10}H_{18}Br_2O_2$: C, 36.39; H, 5.50%.

Methyl (*E*)-3-Fluoro-2-hexylacrylate (4g): Bp 65–69 °C (10 Torr, bath temp); IR (neat) 2954, 2928, 2858, 1730, 1659, 1438, 1284, 1252, 1198, 1149, 1124, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.5 Hz, 3H), 1.20–1.52 (m, 8H), 2.30 (td, *J*=7.3, 2.7 Hz, 2H), 3.75 (s, 3H), 7.53 (d, *J*=82.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.02, 22.54, 23.36 (d, *J*=2.7 Hz), 28.33, 28.88, 31.50, 51.65, 118.56 (d, *J*=11.1 Hz), 157.99 (d, *J*=275.7 Hz), 167.22 (d, *J*=18.6 Hz); ^{19}F NMR ($CDCl_3$) δ -117.36 (dt, *J*=82.7, 3.0 Hz); MS (70 eV) *m/z* (rel intensity) 157 (M^+-OMe, 4), 125 (20), 118 (M^+-C_5H_{10}, 13), 109 (41), 43 (100), 41 (63). Found: C, 63.60; H, 9.29%. Calcd for $C_{10}H_{17}FO_2$: C, 63.81; H, 9.10%.

Methyl 2-(Bromofluoromethyl)octanoate (5g, diastereomeric mixture (55:45)): Bp 81–85 °C (7 Torr, bath temp); IR (neat) 2952, 2926, 2856, 1740, 1458, 1437, 1255, 1217, 1164, 1047, 630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.5 Hz, 3H), 1.30 (bs, 8H), 1.65–1.90 (m, 2H), 3.02–3.27 (m, 1H), 3.76 (s, 3H), 6.53 (dd, *J*=49.8, 7.6 Hz, 0.55H), 6.56 (dd, *J*=49.2, 7.3 Hz, 0.45H); ^{13}C NMR ($CDCl_3$) δ 13.95, 22.46, 26.51, 26.81, 28.50 (d, *J*=3.0 Hz), 28.87, 31.41, 52.19, 54.84 (d, *J*=52.7 Hz), 55.23 (d, *J*=54.8 Hz), 93.37 (d, *J*=256.2 Hz), 94.72 (d, *J*=254.1 Hz), 170.74 (d, *J*=3.9 Hz), 170.88 (d, *J*=10.5 Hz); ^{19}F NMR ($CDCl_3$) δ -134.11 (dd, *J*=49.2, 9.8 Hz, 0.45F), -141.58 (dd, *J*=49.2, 10.8 Hz, 0.55F); MS (70 eV) *m/z* (rel intensity) 189 (M^+-^{79}Br, 25), 157 (6), 109 (14), 106 (5), 105 (100). Found: C, 44.92; H, 6.98%. Calcd for $C_{10}H_{18}BrFO_2$: C, 44.62; H, 6.74%.

Dehydrohalogenation of Octyl 3,3-Dihalopropanoates or Methyl 2-(Dihalomethyl)octanoate. The crude product prepared by the reaction of

ketene silyl acetal **1a** or **1b** (2.0 mmol) with trihalomethane (1.0 mmol) was treated with Et_3N (2 ml) at room temperature. After stirring for 0.5–1 h, the resulting precipitate was filtered through anhydrous Na_2SO_4. The filtrate was concentrated *in vacuo* and the residual oil was submitted to silica-gel column chromatography to give octyl (*E*)-3-haloacrylate. Dehydrohalogenation of methyl 2-(dihalomethyl)-octanoate, derived from the reaction of **1c** with trihalomethane, was slow at room temperature, thus a mixture of the crude product and Et_3N (5 ml) was refluxed for 1–8 h.

1,1,1-Tribromopropane. The title compound was prepared according to the reported procedure[8]: Bp 88–90 °C (44 Torr); IR (neat) 2980, 2934, 1450, 1097, 1075, 909, 813, 705, 618 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.27 (t, *J*=7.0 Hz, 3H), 3.02 (q, *J*=7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.18, 44.50, 53.63; MS (70 eV) *m/z* (rel intensity) 203 (M^++4-^{79}Br, 48), 201 (M^++2-^{79}Br, 100), 199 (M^+-^{79}Br, 52), 121 (M^++2-^{79}Br-H^{79}Br, 55), 119 (M^+-^{79}Br-H^{79}Br, 57), 39 (78). Found: C, 13.10; H, 1.87%. Calcd for $C_3H_5Br_3$: C, 12.83; H, 1.79%.

Octyl (*E*)-3-Bromo-2-pentenoate ((*E*)-6): The stereochemistry of (*E*) or (*Z*)-**6** was assigned by the chemical shift of allylic protons. Allylic protons of (*E*)-**6** appear at lower field (δ 3.15) compared to those of (*Z*)-**6** (δ 2.62) due to deshield by carbonyl group. Bp 87–91 °C (1 Torr, bath temp); IR (neat) 2952, 2924, 2854, 1721, 1626, 1459, 1342, 1304, 1181, 1104 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1.19 (t, *J*=7.4 Hz, 3H), 1.28 (bs, 10H), 1.58–1.73 (m, 2H), 3.15 (q, *J*=7.3 Hz, 2H), 4.10 (t, *J*=6.7 Hz, 2H), 6.31 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.09, 14.06, 22.61, 25.91, 28.54, 29.16 (two peaks), 31.55, 31.75, 64.62, 122.52, 151.66, 164.30; MS (70 eV) *m/z* (rel intensity) 292 (M^++2, 2.4), 290 (M^+, 2.9), 211 (M^+-^{79}Br, 20), 181 (18), 180 (M^++2-C_8H_{15}, 35), 179 (16), 178 (M^+-C_8H_{15}, 34), 163 (38), 161 (33), 99 (100). Found: C, 53.72; H, 8.12%. Calcd for $C_{13}H_{23}BrO_2$: C, 53.62; H, 7.96%.

Octyl (*Z*)-3-Bromo-2-pentenoate ((*Z*)-6): Bp 94–98 °C (1 Torr, bath temp); IR (neat) 2952, 2924, 2852, 1733, 1637, 1459, 1292, 1246, 1172 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.5 Hz, 3H), 1.19 (t, *J*=7.4 Hz, 3H), 1.28 (bs, 10H), 1.60–1.75 (m, 2H), 2.62 (qd, *J*=7.4, 1.1 Hz, 2H), 4.15 (t, *J*=6.7 Hz, 2H), 6.30 (t, *J*=1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.06, 14.03, 22.58, 25.90, 28.52, 29.13 (two peaks), 31.72, 37.02, 64.63, 118.41, 143.32, 164.40; MS (70 eV) *m/z* (rel intensity) 211 (M^+-^{79}Br, 2), 181 (M^++2-C_8H_{15}, 43), 179 (M^+-C_8H_{15}, 43), 163 (35), 161 (30), 55 (54), 53 (66), 43 (87), 41 (100). Found: C, 53.40; H, 8.11%. Calcd for $C_{13}H_{23}BrO_2$: C, 53.62; H, 7.96%.

Octyl 3, 3-Dibromopentanoate (7): Bp 111–115 °C (2 Torr, bath temp); IR (neat) 2952, 2926, 2854, 1741, 1342, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.4 Hz, 3H), 1.23 (t, *J*=7.1 Hz, 3H), 1.27 (bs, 10H), 1.60–1.74 (m, 2H), 2.63 (q, *J*=7.1 Hz, 2H), 3.60 (s, 2H), 4.14 (t, *J*=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 12.29, 14.06, 22.60, 25.85, 28.45, 29.11 (two peaks), 31.72, 43.02, 53.90, 65.30, 67.41, 167.76; MS (70 eV) *m/z* (rel intensity) 293 (M^++2-^{79}Br, 0.4), 292 (M^++2-$H^{79}Br$, 0.4), 291 (M^+-^{79}Br, 0.5), 290 (M^+-$H^{79}Br$, 0.2), 263 (M^++4-C_8H_{15}, 0.2), 261 (M^++2-C_8H_{15}, 0.6), 259 (M^+-C_8H_{15}, 0.2), 181 (24), 179 (21), 71 (54), 57 (90), 43 (100), 41 (74). Found: C, 42.25; H, 6.76%. Calcd for $C_{13}H_{24}Br_2O_2$: C, 41.96; H, 6.50%.

Ethyl Octyl Fumarate (8): Bp 92–96 °C (2 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1725, 1297, 1260, 1173, 1154, 1033, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J*=6.4 Hz, 3H), 1.25–1.43 (m, 13H), 1.62–1.76 (m, 2H), 4.20 (t, *J*=6.7 Hz, 2H), 4.27 (q, *J*=7.1 Hz, 2H), 6.86 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04 (two peaks), 22.58, 25.82, 28.44, 29.11 (two peaks), 31.71, 61.26, 65.44, 133.51, 133.60, 164.94, 165.02; MS (70 eV) *m/z* (rel intensity) 211 (M^+-OEt, 20), 146 (10), 145 (M^+-C_8H_{15}, 100), 128 (38), 127 (M^+-C_8H_{15}-H_2O, 85), 117 (57), 112 (24), 100 (22), 99 (52), 70 (79), 69 (68), 56 (77), 55 (99), 43 (79), 41 (83). Found:

C, 65.56 ; H, 9.62%. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44%.

1-Ethyl 4-Octyl 2-Bromosuccinate (9): Bp 102–106 °C (0.71 Torr, bath temp); IR (neat) 2952, 2926, 2854, 1741, 1333, 1302, 1260, 1207, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.3 Hz, 3H), 1.25–1.40 (m, 13H), 1.55–1.70 (m, 2H), 2.98 (dd, *J*=17.1, 6.3 Hz, 1H), 3.27 (dd, *J*=17.1, 8.8 Hz, 1H), 4.11 (t, *J*=6.7 Hz, 2H), 4.26 (q, *J*=7.2 Hz, 2H), 4.56 (dd, *J*=8.8, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.85, 14.04, 22.60, 25.78, 28.46, 29.12 (two peaks), 31.73, 38.31, 39.77, 62.25, 65.39, 169.01, 169.66; MS (70 eV) *m/z* (rel intensity) 227 (M^++2-C_8H_{15}, 4), 225 (M^+-C_8H_{15}, 6), 209 (M^++2-C_8H_{15}-H_2O, 15), 207 (M^+-C_8H_{15}-H_2O, 12), 181 (8), 179 (9), 57 (58), 56 (60), 55 (74), 43 (98), 41 (100). Found: C, 50.12; H, 7.58%. Calcd for $C_{14}H_{25}BrO_4$: C, 49.86; H, 7.47%.

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CHAPTER 5

Triethylborane Induced Stereoselective Radical Addition of R_3SiH to Acetylenes and Stereoselective Reduction of Alkenyl Iodides with Tris(trimethylsilyl)silane

Triethylborane induced radical addition of various organosilanes (R_3SiH) to acetylenes has been studied. Among them, tris(trimethylsilyl)silane (TTMSS) proved to be the best reagent for the hydrosilylation of acetylenic compounds in terms of yield and stereoselectivity. For instance, reaction of 1-dodecyne with TTMSS at room temperature for 3 h under Et_3B catalyst provided (*Z*)-1-tris(trimethylsilyl)silyl-1-dodecene selectively in 98% yield. The stereochemical course of reduction of alkenyl iodides with TTMSS-Et_3B or *n*-Bu_3SnH-Et_3B has been examined. Treatment of 1-dimethylphenylsilyl-2-iodo-1-dodecene with TTMSS-Et_3B at room temperature afforded (*Z*)-1-dimethylphenylsilyl-1-dodecene selectively (*Z*/*E* > 30/1). On the other hand, treatment with *n*-Bu_3SnH-Et_3B gave (*E*)-1-dimethylphenylsilyl-1-dodecene exclusively.

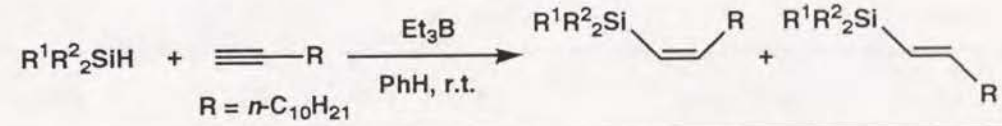
(1) Triethylborane Induced Stereoselective Radical Addition of R_3SiH to Carbon-Carbon Triple Bonds. Transition metal catalyzed hydrosilylation of acetylenes has been extensively studied and widely used for the preparation of alkenylsilanes.[1] In contrast, the synthetic use of hydrosilylation reaction catalyzed by various radical initiators such as peroxides and AIBN has serious limitations. Low stereoselectivity of the reaction is one of difficult problems. In addition, the choice of hydrosilanes is limited to silanes such as Cl_3SiH, $MeCl_2SiH$ and Ph_3SiH because trialkylsilanes (Me_3SiH and Et_3SiH) can not donate hydrogen to alkenyl radicals efficiently.[2]

We have reported that Et_3B facilitates the addition of Ph_3SnH[3] or Ph_3GeH[4] to acetylenes in the presence of oxygen. Hydrostannylation of 1-dodecyne with Ph_3SnH-Et_3B provided a 7/3–8/2 mixture of (*E*)-and (*Z*)-1-triphenylstannyl-1-dodecene irrespective of the reaction conditions.[3] In contrast, Et_3B induced hydrogermylation of 1-dodecyne with Ph_3GeH gave (*E*)- or (*Z*)-1-triphenylgermyl-1-dodecene with excellent control of stereochemistry under equilibrating conditions or non-equilibrating conditions.[4] Whereas the reaction at -78 °C afforded (*Z*)-1-triphenylgermyl-1-dodecene exclusively, the addition at 60 °C provided (*E*)-1-triphenylgermyl-1-dodecene as a single product. Here we wish to report that Et_3B mediated hydrosilylation of carbon-carbon triple bonds with a variety of organosilanes (R_3SiH) and that treatment of terminal acetylenes with tris(trimethylsilyl)silane (TTMSS)[5] in the presence of a catalytic amount of Et_3B gave (*Z*)-1-tris(trimethylsilyl)silyl-1-alkenes with high stereoselectivity.

Triethylborane induced hydrosilylation of acetylenes with Ph_3SiH proceeded very sluggishly as compared to hydrogermylation with Ph_3GeH and hydrostannylation with Ph_3SnH. Stirring a hexane solution of 1-dodecyne (1.0 mmol) and Ph_3SiH (2.0 mmol) in the presence of Et_3B (2.0 mmol) at room temperature for 88 h gave a mixture of (*Z*)- and (*E*)-1-triphenylsilyl-1-dodecene only in 42% yield

(*Z*/*E* = 12/1). Then, hydrosilylation of 1-dodecyne was examined using various silanes such as Ph_2SiH_2, $Me_3SiSiPh_2H$, $(Me_3Si)_2SiPhH$, and $(Me_3Si)_3SiH$ (TTMSS). Reaction of each silane with 1-dodecyne at room temperature in the presence of Et_3B provided the corresponding hydrosilylation products in poor to excellent yields. The results are shown in Table 1. Reaction with Ph_2SiH_2 was as slow as the hydrosilylation with Ph_3SiH and gave respective alkenylsilane in low yield in spite of the use of excess amount of silane and Et_3B even after prolonged reaction time (70–75 h). Substitution of phenyl group of Ph_3SiH by trimethylsilyl group facilitated the free-radical hydrosilylation. Treatment of 1-dodecyne with $Me_3SiSiPh_2H$ or $(Me_3Si)_2SiPhH$ provided 1-[diphenyl(trimethylsilyl)silyl]-1-dodecene or 1-[bis(trimethylsilyl)phenylsilyl]-1-dodecene in good yield with high stereoselectivity (*Z*/*E* = 15/1 or 16/1). TTMSS proved to be the best reagent and afforded (*Z*)-1-[tris(trimethylsilyl)silyl]-1-dodecene (**1**) in 98% yield ((*Z*)-isomer **1**/(*E*)-isomer **2** = 17/1)[6]. The reaction at room temperature completed within 3 h in the presence of a catalytic amount of Et_3B.

Table 1. Hydrosilylation of 1-dodecyne with various silanes



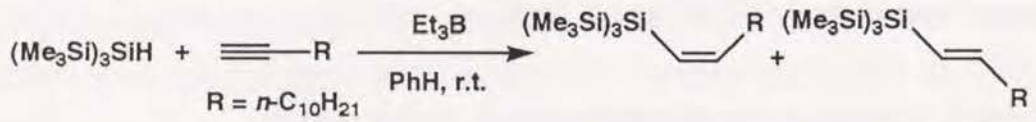
Entry	$R^1R^2_2SiH$ (mmol)		Et_3B / mmol	Time / h	Yield / %	*Z* / *E* [a]
1	Ph_3SiH	(2.0)	2.0	88	42	12 / 1
2	Ph_2SiH_2	(2.0)	2.0	75	20	2.4 / 1
3	$Me_3SiSiPh_2H$	(1.1)	1.0	44	78	16 / 1
4	$(Me_3Si)_2SiPhH$	(1.1)	0.1	12	74	15 / 1
5	$(Me_3Si)_3SiH$	(1.1)	0.1	3	98	17 / 1

a) The stereoisomeric ratios were determined by the examination of ^1H NMR of isolated products.

The stereoisomeric ratio of **1** to **2** depended on the reaction conditions. Whereas heating a benzene solution of 1-dodecyne (1.0 mmol) and TTMSS (1.1 mmol) at reflux for 30 min in the presence of AIBN (0.1 mmol) gave a mixture of (*Z*)-isomer **1** and (*E*)-isomer **2** (**1**/**2** = 4/1) in 98% combined yield, Et_3B initiated reaction in toluene at 0 °C provided **1** almost exclusively (96% yield, **1**/**2** > 20/1).

Next, Et_3B induced hydrosilylation of various alkynes with TTMSS at room temperature has been examined. Monosubstituted acetylenes provided the corresponding tris(trimethylsilyl)silyl substituted alkenes in good to excellent yields with high stereoselectivity (Table 2). In the case of phenylacetylene or ethyl propiolate, only (*Z*)-isomeric product was observed in the reaction mixture. Internal acetylene such as 6-dodecyne did not undergo hydrosilylation with TTMSS, and starting material was recovered unchanged under the same reaction conditions.

Table 2. Hydrosilylation of alkynes with TTMSS[a)]

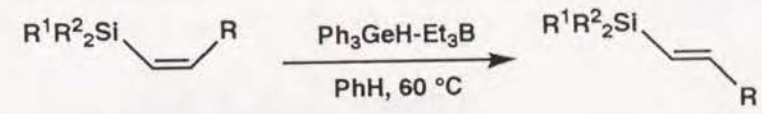


Entry	R	Time / h	Yield / %	*Z* / *E* [b)]
1	n-$C_{10}H_{21}$	3	98	17 / 1
2	Ph	3	91	>50 / 1
3	COOEt	3	90	>50 / 1
4	CH_2OH	5	50	17 / 1
5	CH_2OTHP	5	72	>20 / 1
6	CH_2CH_2OH	5	81	>20 / 1

a) $(Me_3Si)_3SiH$ (1.1 mmol), acetylene (1.0 mmol), and Et_3B (0.1 mmol) were employed. b) The stereoisomeric ratios were determined by the examination of ^1H NMR of isolated products.

The isomerization of (*Z*)-1-tris(trimethylsilyl)silyl-1-alkenes into (*E*)-isomers by addition-elimination sequences of tris(trimethylsily)silyl radical did not proceed. Heating a mixture of **1** and TTMSS at 60 °C for 15 h gave only a small amount of (*E*)-isomer **2** (< 5%) along with recovered **1**. This shows sharp contrast to a facile isomerization of (*Z*)-1-triphenylgermyl-1-dodecene or (*Z*)-1-triphenylstannyl-1-dodecene which was partially or completely isomerized to the corresponding (*E*)-isomers[7)] at room temperature upon treatment with Ph_3GeH-Et_3B or Ph_3SnH-Et_3B. (*Z*)-Alkenylsilane **1** was completely isomerized to (*E*)-isomer **2** at 60 °C by the use of Ph_3GeH-Et_3B[4)] which is shown in Table 3 along with other examples. Thus, the procedure provides us with a synthetic method for the preparation of both (*Z*)- and (*E*)-alkenylsilanes.

Table 3. Isomerization of Alkenylsilane by Ph_3GeH-Et_3B

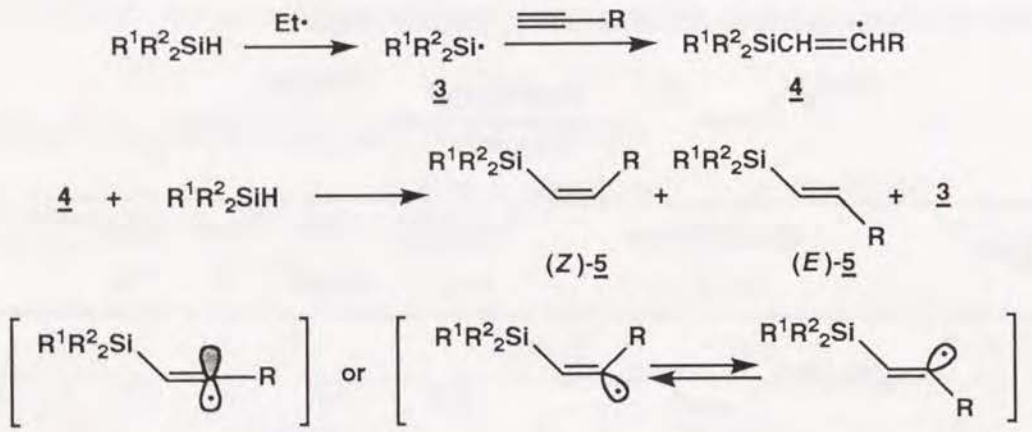


Entry	Alkenylsilane (*Z* / *E*)	Ph_3GeH / equiv	Et_3B / equiv	Time / h	Yield / %	*Z* / *E* [a)]
1	$Ph_2(Me_3Si)Si$, n-$C_{10}H_{21}$ (16 / 1)	0.2	0.2	16	97	< 1 / 20
2	$Ph(Me_3Si)_2Si$, n-$C_{10}H_{21}$ (12 / 1)	0.5	0.5	16	91	1 / 16
3	$(Me_3Si)_3Si$, n-$C_{10}H_{21}$ (> 20 / 1)	0.5	0.5	15	90	< 1 / 30
4	$(Me_3Si)_3Si$, CH_2CH_2OH (17 / 1)	0.5	0.5	15	76	< 1 / 20

a) The stereoisomeric ratios were determined by the examination of ^1H NMR.

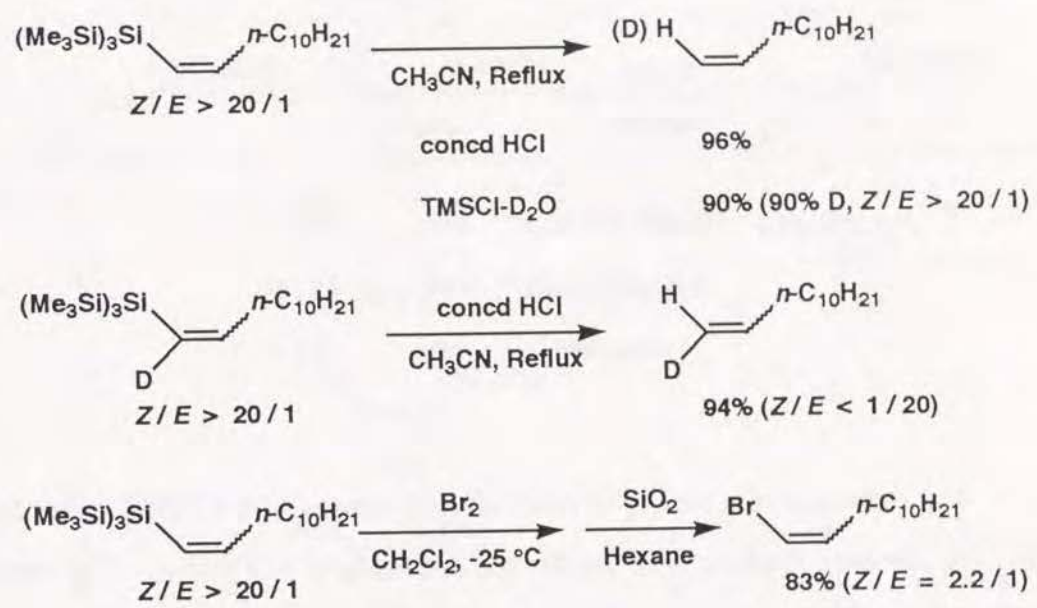
We assume following reaction mechanism for the hydrosilylation of terminal acetylenes with $R^1R^2{}_2SiH$ (Scheme 1). Ethyl radical, generated by the attack of oxygen on triethylborane, abstracts hydrogen from silane to give silyl radical ($R^1R^2{}_2Si\cdot$, **3**). The silyl radical adds to terminal acetylenic carbon to provide alkenyl radical **4** which abstracts hydrogen from silane to produce alkenylsilane **5** as a mixture of (*Z*)- and (*E*)-isomer under regeneration of silyl radical **3**. The selective formation of (*Z*)-alkenylsilane is due to steric hindrance of silyl group which prevents the *syn* attack of silane in the π-radical or in the pair of σ-radicals.[8)]

Scheme 1.



Hydrodesilylation of **1** with concd HCl proceeded in acetonitrile (Scheme 2). Treatment of **1** with TMSCl-D_2O instead of concd HCl gave (*Z*)-1-deuterio-1-dodecene selectively. Moreover, the reaction of (*Z*)-1-deuterio-1-[tris(trimethylsilyl)silyl]-1-dodecene with concd HCl formed (*E*)-1-deuterio-1-dodecene exclusively. These results indicate that hydrodesilylation of **1** proceeds with retention of stereochemistry[9)]. On the other hand, bromodesilylation of **1** gave 1-bromo-1-dodecene under low stereocontrol ($Z/E = 2.2/1$)[10)].

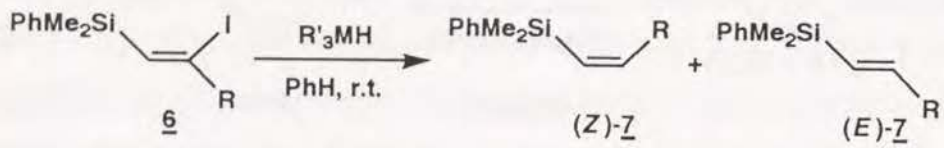
Scheme 2.



(2) Reduction of Alkenyl Iodides with TTMSS

It was anticipated that reduction of 1-silyl-2-iodo-1-alkenes with TTMSS would proceed *via* the same alkenyl radical as **4** in Scheme 1 and provide the same stereoisomeric mixtures of (*Z*)-alkenylsilane and (*E*)-alkenylsilane as hydrosilylation of acetylenes. This was indeed the case as indicated by the following experiments. Treatment of 1-dimethylphenylsilyl-2-iodo-1-dodecene **6** with TTMSS in the presence of Et_3B catalyst at room temperature afforded (*Z*)-1-dimethylphenylsilyl-1-dodecene ((**Z**)-**7**) selectively (Z/E > 30/1). In contrast, reduction of **6** with *n*-Bu_3SnH without Et_3B gave a mixture of (*Z*)- and (*E*)-1-dimethylphenylsilyl-1-dodecene (Z/E = 2.7/1). Moreover, treatment of **6** with *n*-Bu_3SnH-Et_3B afforded (***E***)-**7** exclusively.[7)] In these two experiments, a primary product (**Z**)-**7** isomerized to thermodynamically more stable (***E***)-**7** by the addition-elimination sequences of *n*-Bu_3Sn radical (Scheme 3).

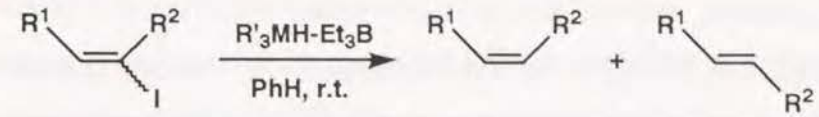
Scheme 3.

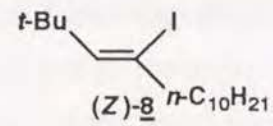
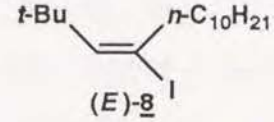
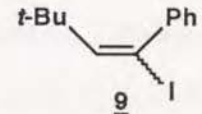
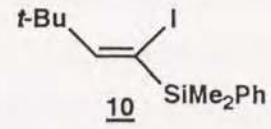
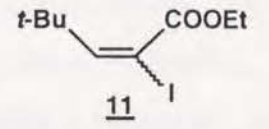
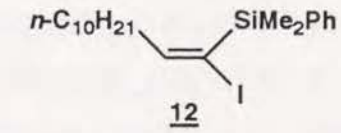
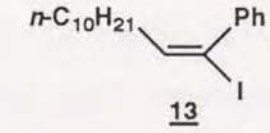


R = *n*-$C_{10}H_{21}$	$(Me_3Si)_3SiH$-Et_3B	84%	> 30 / 1
	n-Bu_3SnH-Et_3B	97%	< 1 / 20
	n-Bu_3SnH	96%	2.7 / 1

The reduction of a variety of other alkenyl iodides with TTMSS under Et_3B catalyst has been studied. The results are summarized in Table 4. The stereochemical results by the reduction with *n*-Bu_3SnH-Et_3B are also shown in the Table. Reduction with TTMSS-Et_3B system produced (*Z*)-alkenes selectively. On the other hand, *n*-Bu_3SnH-Et_3B gave (*E*)-alkenes as main products. It is worth to note several points. (1) The stereochemical outcome of the reduction with TTMSS-Et_3B was independent on the stereochemistry of starting material. For instance, treatment of (*E*)-2,2-dimethyl-4-iodo-3-tetradecene ((***E*-8**) or (*Z*)-2,2-dimethyl-4-iodo-3-tetradecene ((***Z*-8**) with TTMSS-Et_3B at room temperature for 2h provided the same isomeric mixture of (*Z*)-2,2-dimethyl-3-tetradecene and (*E*)-isomer (*Z*/*E* = 2.1/1). Thus, the reduction proceeds through the same intermediary alkenyl radical *t*-BuCH=$\dot{C}$(*n*-$C_{10}H_{21}$). (2) Comparison of the reduction of **9** with **13** (Entry 4 with 12) and **10** with **12** (Entry 6 with 10) shows that (*Z*)-selectivity in the reaction with TTMSS-Et_3B increased with increase of the bulkiness of R^1 group. (3) In the reaction with *n*-Bu_3SnH-Et_3B, the presence of Ph, $PhMe_2Si$, or COOEt group which stabilizes α-carbon radical[11] increases (*E*)-selectivity because of the facile isomerization by addition-elimination of *n*-Bu_3Sn radical.

Table 4. Reduction of Alkenyl Iodides with Tris(trimethylsilyl)silane



Entry	Substrate	Method[a]	Yield / %	*Z* / *E*[b]
1		A	97	2.1 / 1
2	(*Z*)-**8**	B	98	1 / 2.8
3		A	99	2.1 / 1
	(*E*)-**8**			
4		A	77	>60 / 1
5	**9**	B	75	9 / 1
6		A	94	>100 / 1
7	**10**	B	99	1 / 3.4
8		A	70	5.7 / 1
9	**11**	B	77	<1 / 100
10		A	96	5.8 / 1
11	**12**	B	95	1 / 15
12		A	87	4.0 / 1
13	**13**	B	94	1 / 3.7

a) Method A: TTMSS (1.1 equiv)-Et_3B (0.1 equiv), Method B: *n*-Bu_3SnH (1.1 equiv)-Et_3B (0.1 equiv) b) The stereoisomeric ratios of products were determined by the examination of ^1H NMR.

In conclusion, the addition of TTMSS to acetylenes provides us with a stereoselective synthetic method for (*Z*)-1-[tris(trimethylsilyl)silyl]-1-alkenes, since TTMSS radical can not cause the isomerization of the resulting (*Z*)-alkenes into (*E*)-alkenes. Meantime, (*E*)-1-[tris(trimethylsilyl)silyl]-1-alkenes are produced on treatment of (*Z*)-1-[tris(trimethylsilyl)silyl]-1-alkenes with Ph_3GeH-Et_3B. Reduction of 1,2-disubstituted-1-iodo-1-alkenes with TTMSS-Et_3B affords (*Z*)-1,2-disubstituted-1-alkenes selectively.

Experimental

General Procedure for Et_3B Induced Hydrosilylation of 1-dodecyne with Ph_3SiH, Ph_2SiH_2, or $Me_3SiSiPh_2H$. Hydrosilylation of 1-dodecyne with Ph_3SiH is representative. A hexane solution of Et_3B (0.96 M, 2.1 mL, 2.0 mmol) was added to a mixture of 1-dodecyne (0.166 g, 1.00 mmol) and Ph_3SiH (0.520 g, 2.00 mmol) at room temperature under argon atmosphere. After stirring for 88 h, the reaction mixture was concentrated and distilled to remove 1-dodecyne and Ph_3SiH *in vacuo* (0.50 Torr, bath temp, 120 °C, 1 h). The residual oil was purified by silica-gel column chromatography using hexane as an eluent to give 1-triphenylsilyl-1-dodecene (0.179 g) in 42% yield.

(*Z*)-1-(Triphenylsilyl)-1-dodecene: Bp 160–164 °C (0.27 Torr, bath temp); IR (neat) 3062, 2920, 2850, 1602, 1428, 1110, 712, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85–1.32 (m, 19H, included 0.88 (t, *J*=6.9 Hz)), 1.86–1.95 (m, 2H), 6.02 (dt, *J*=14.0, 1.3 Hz, 1H), 6.71 (dt, *J*=14.0, 7.5 Hz, 1H), 7.31–7.42 (m, 9H), 7.54–7.59 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 14.14, 22.70, 29.04, 29.19, 29.33, 29.51, 31.91, 34.57, 122.52, 127.80, 129.28, 135.64, 135.71, 154.06; Found: C, 84.34; H, 9.04%. Calcd for $C_{30}H_{38}Si$: C, 84.44; H, 8.98%.

(*Z*)-1-(Diphenylsilyl)-1-dodecene: Bp 139–143 °C (0.55 Torr, bath temp); IR (neat) 2952, 2920, 2850, 2120, 1603, 1429, 1115, 800, 730, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.8 Hz, 3H), 1.15–1.36 (m, 16H), 2.15–2.23 (m, 2H), 5.27 (d, *J*=5.3 Hz, 1H), 5.83 (ddt, *J*=13.8, 5.4, 1.2 Hz, 1H), 6.66 (dt, *J*=13.8, 7.4 Hz, 1H), 7.31–7.42 (m, 6H), 7.54–7.60 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.14, 22.69, 29.14, 29.23. 29.34, 29.42, 29.57 (two peaks), 31.91, 33.76, 121.31, 127.97, 129.44, 134.57, 135.23, 153.74; MS (70 eV) *m/z* (rel intensity) 351 (M^++1, 0.3), 350 (M^+, 1.4), 184 (20), 183 (100), 182 (30), 181 (24), 107 (15), 105 (34). Found: C, 82.44; H, 9.83%. Calcd for $C_{24}H_{34}Si$: C, 82.21; H, 9.77%.

(*E*)-1-(Diphenylsilyl)-1-dodecene: Bp 139–143 °C (0.55 Torr, bath temp); IR (neat) 2950, 2922, 2850, 2116, 1615, 1429, 1114, 807, 727, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=6.7 Hz, 3H), 1.18–1.48 (m, 16H), 2.16–2.23 (m, 2H), 5.08 (d, *J*=3.1 Hz, 1H), 5.92 (ddt, *J*=18.5, 3.1, 1.5 Hz, 1H), 6.29 (dt, *J*=18.5, 6.2 Hz, 1H), 7.32–7.43 (m, 6H), 7.54–7.60 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.14, 22.69, 28.41, 29.19, 29.35, 29.47, 29.61 (two peaks), 31.91, 36.97, 121.78, 127.92, 129.53, 134.24, 135.40, 154.03; MS (70 eV) *m/z* (rel intensity) 351 (M^++1, 0.5), 350 (M^+, 1.9), 184 (20), 183 (100), 182 (33), 181 (24), 107 (15), 105 (29). Found: C, 82.38; H, 9.93%. Calcd for $C_{24}H_{34}Si$: C, 82.21; H, 9.77%.

(*Z*)-1-[Diphenyl(trimethylsilyl)silyl]-1-dodecene: Bp 145–149 °C (0.33 Torr, bath temp); IR (neat) 2950, 2922, 2850, 1598, 1428, 1244, 1102, 851, 834, 736, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9H), 0.88 (t, *J*=6.9 Hz, 3H), 0.98–1.32 (m, 16H), 1.85–1.92 (m, 2H), 5.84 (dt, *J*=13.6, 1.2 Hz, 1H), 6.60 (dt, *J*=13.6, 7.3 Hz, 1H), 7.28–7.36 (m, 6H), 7.45–7.53 (m, 4H); ^{13}C NMR ($CDCl_3$) δ -1.21, 14.15, 22.70, 29.20, 29.29, 29.41, 29.52, 31.91, 34.92, 122.97, 127.81, 128.57, 135.28, 136.71, 152.49; MS (70 eV) *m/z* (rel intensity) 423 (M^++1, 1.4), 422 (M^+, 2.2), 349 (36), 287 (68), 197 (53), 183 (100), 135 (50), 121 (38), 107 (18), 105 (43). Found: C, 76.41; H, 10.01%. Calcd for $C_{27}H_{42}Si_2$: C, 76.70; H, 10.01%.

(*E*)-1-[Diphenyl(trimethylsilyl)silyl]-1-dodecene: Bp 141–145 °C (0.21 Torr, bath temp); IR (neat) 2920, 2850, 1428, 1244, 1103, 852, 834, 735, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 9H), 0.88 (t, *J*=6.7 Hz, 3H), 1.20–1.44 (m, 16H), 2.16–2.23 (m, 2H), 5.94 (dt, *J*=18.5, 1.2 Hz, 1H), 6.11 (dt, *J*=18.5, 6.1 Hz, 1H), 7.29–7.38 (m, 6H), 7.44–7.51 (m, 4H); ^{13}C NMR ($CDCl_3$) δ -1.31, 14.14, 22.70, 28.71, 29.14, 29.36, 29.48, 29.62, 29.65, 31.92, 37.19, 123.74, 127.79, 128.68, 135.52, 136.35, 151.94; MS (70 eV) *m/z* (rel intensity) 424 (M^++2, 0.6), 423 (M^++1, 1.5), 422 (M^+, 2), 349 (31), 287 (61), 197 (52), 183 (100), 135 (36),

121 (25), 105 (25). Found: C, 76.65; H, 9.80%. Calcd for $C_{27}H_{42}Si_2$: C, 76.70; H, 10.01%.

General Procedure for Et_3B Induced Hydrosilylation of Acetylenes with $(Me_3Si)_2SiPhH$ or $(Me_3Si)_3SiH$. Typical procedure is as follows. Under argon atmosphere, Et_3B (0.96 M hexane solution, 0.10 mL, 0.10 mmol) was added to a solution of 1-dodecyne (0.166 g, 1.00 mmol) and $(Me_3Si)_3SiH$ (0.274 g, 1.10 mmol) in benzene (2.0 mL) at room temperature. After stirring for 3 h, the reaction mixture was concentrated *in vacuo*. Purification by silica-gel column (hexane) yielded 1-[tris(trimethylsilyl)silyl]-1-dodecene (0.407 g, 98%, *Z*/*E* = 17/1).

(*Z*)-1-[Phenylbis(trimethylsilyl)silyl]-1-dodecene: Bp 128–132 °C (0.35 Torr, bath temp); IR (neat) 2952, 2922, 2850, 1244, 835, 697, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 (s, 18H), 0.88 (t, *J*=6.8 Hz, 3H), 1.14–1.35 (m, 16H), 1.91–1.99 (m, 2H), 5.67 (dt, *J*=13.3, 1.3 Hz, 1H), 6.53 (dt, *J*=13.3, 7.2 Hz, 1H), 7.25–7.31 (m, 3H), 7.40–7.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -0.49, 14.15, 22.70, 29.32, 29.48, 29.54, 31.91, 35.39, 121.37, 127.60, 135.12, 136.96, 151.11; MS (70 eV) *m/z* (rel intensity) 419 (M^++1, 1.0), 418 (M^+, 2.5), 179 (26), 178 (53), 163 (19), 135 (99), 121 (41), 116 (36), 73 (100). Found: C, 69.05; H, 11.36%. Calcd for $C_{24}H_{46}Si_3$: C, 68.82; H, 11.07%.

(*E*)-1-[Phenylbis(trimethylsilyl)silyl]-1-dodecene: Bp 125–129 °C (0.30 Torr, bath temp); IR (neat) 2948, 2922, 2850, 1244, 835, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 (s, 18H), 0.88 (t, *J*=6.7 Hz, 3H), 1.18–1.47 (m, 16H), 2.15–2.22 (m, 2H), 5.77 (dt, *J*=18.4, 1.4 Hz, 1H), 6.13 (dt, *J*=18.4, 6.5 Hz, 1H), 7.26–7.32 (m, 3H), 7.40–7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -0.66, 14.14, 22.69, 29.00, 29.07, 29.36, 29.48, 29.62, 29.67, 31.92, 37.47, 122.63, 127.65, 127.75, 135.21, 136.80, 150.50; MS (70 eV) *m/z* (rel intensity) 419 (M^++1, 1.0), 418 (M^+, 1.9), 193 (19), 179 (30), 178 (54), 163 (21), 135 (100), 121 (40), 116 (35), 73 (99). Found: C, 68.59; H, 11.25%. Calcd for $C_{24}H_{46}Si_3$: C, 68.82; H, 11.07%.

(*Z*)-1-[Tris(trimethylsilyl)silyl]-1-dodecene: Bp 127–131 °C (0.38 Torr, bath temp); IR (neat) 2948, 2922, 2850, 1244, 832, 686, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 27H), 0.88 (t, *J*=6.7 Hz, 3H), 1.22–1.41 (m, 16H), 2.03–2.10 (m, 2H), 5.47 (dt, *J*=13.0, 1.5 Hz, 1H), 6.38 (dt, *J*=13.0, 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.09, 14.15, 22.70, 29.33, 29.59, 29.69, 29.80, 31.91, 35.65, 119.55, 149.48; MS (70 eV) *m/z* (rel intensity) 415 (M^++1, 0.6), 414 (M^+, 1.7), 175 (16), 174 (68), 131 (12), 129 (12), 117 (11), 73 (100). Found: C, 60.51; H, 11.87%. Calcd for $C_{21}H_{50}Si_4$: C, 60.78; H, 12.14%.

(*E*)-1-[Tris(trimethylsilyl)silyl]-1-dodecene: Bp 116–120 °C (0.33 Torr, bath temp); IR (neat) 2946, 2922, 2850, 1244, 832, 685, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 27H), 0.88 (t, *J*=6.7 Hz, 3H), 1.21–1.39 (m, 16H), 2.05–2.13 (m, 2H), 5.47 (dt, *J*=18.2, 1.3 Hz, 1H), 5.97 (dt, *J*=18.2, 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.78, 14.14, 22.69, 28.99, 29.18, 29.35, 29.47, 29.61, 29.67, 31.92, 37.64, 120.36, 149.50; MS (70 eV) *m/z* (rel intensity) 416 (M^++2, 0.5), 415 (M^++1, 0.7), 414 (M^+, 2.0), 189 (11), 175 (21), 174 (76), 131 (14), 129 (13), 117 (14), 73 (100). Found: C, 60.60; H, 12.35%. Calcd for $C_{21}H_{50}Si_4$: C, 60.78; H, 12.14%.

(*Z*)-1-Deuterio-1-[tris(trimethylsilyl)silyl]-1-dodecene: Bp 130–134 °C (0.40 Torr, bath temp); IR (neat) 2946, 2922, 2850, 1244, 834, 685, 615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 27H), 0.88 (t, *J*=6.7 Hz, 3H), 1.22–1.40 (m, 16H), 2.03–2.10 (m, 2H), 6.38 (t, *J*=7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.09, 14.14, 22.70, 29.33, 29.59, 29.69, 29.80, 31.91, 35.61, 119.19 (t, *J*=21.4 Hz), 149.38; MS (70 eV) *m/z* (rel intensity) 416 (M^++1, 0.6), 415 (M^+, 1.6), 175 (20), 174 (70), 131 (10), 117 (11), 73 (100). Found: C, 60.38; H, 11.84; D, 0.47%. Calcd for $C_{21}H_{49}DSi_4$: C, 60.64; H, 11.87; D, 0.48%.

(*E*)-1-Deuterio-1-[tris(trimethylsilyl)silyl]-1-dodecene: Bp 116–120 °C (0.30 Torr, bath temp); IR (neat) 2946, 2922, 2852, 1244, 835, 686, 621 cm^{-1}; ^1H

NMR ($CDCl_3$) δ 0.16 (s, 27H), 0.88 (t, *J*=6.7 Hz, 3H), 1.21–1.38 (m, 16H), 2.06–2.12 (m, 2H), 5.93–5.99 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 0.79, 14.14, 22.70, 28.99, 29.18, 29.36, 29.48, 29.62, 29.68, 31.92, 37.57, 119.99 (t, *J*=21.2 Hz), 149.43 (t, *J*=4.6 Hz); MS (70 eV) *m/z* (rel intensity) 416 (M^++1, 0.6), 415 (M^+, 1.8), 176 (11), 175 (19), 174 (74), 131 (10), 73 (100). Found: C, 60.54; H, 11.74; D, 0.47%. Calcd for $C_{21}H_{49}DSi_4$: C, 60.64; H, 11.87; D, 0.48%.

(*Z*)-3-[Tris(trimethylsilyl)silyl]-2-propen-1-ol: Mp 105–107 °C (Hexane); IR ($CDCl_3$) 3610, 2948, 2890, 1246, 1005, 922, 836, 714, 707, 687, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 27H), 1.42 (bs, 1H), 4.14 (dd, *J*=6.6, 1.1 Hz, 2H), 5.78 (dt, *J*=13.2, 1.1 Hz, 1H), 6.56 (dt, *J*=13.2, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.89, 65.00, 124.90, 146.27; MS (20 eV) *m/z* (rel intensity) 233 (M^++2-$SiMe_3$, 2), 232 (M^++1-$SiMe_3$, 5), 231 (M^+-$SiMe_3$, 18), 215 (46), 157 (16), 141 (17), 131 (26), 117 (20), 73 (100). Found: C, 47.20; H, 10.33%. Calcd for $C_{12}H_{32}OSi_4$: C, 47.30; H, 10.58%.

(*E*)-3-[Tris(trimethylsilyl)silyl]-2-propen-1-ol: Mp 76–78 °C (Hexane); IR ($CDCl_3$) 3608, 2946, 2890, 1245, 1074, 984, 837, 758, 731, 728, 687, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 27H), 1.47 (bs, 1H), 4.15 (dd, *J*=4.9, 1.6 Hz, 2H), 5.84 (dt, *J*=18.5, 1.6 Hz, 1H), 6.18 (dt, *J*=18.5, 4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.76, 66.41, 122.73, 146.38; MS (20 eV) *m/z* (rel intensity) 231 (M^+-$SiMe_3$, 2.7), 215 (28), 199 (29), 175 (32), 141 (32), 131 (55), 117 (33), 73 (100). Found: C, 47.16; H, 10.70%. Calcd for $C_{12}H_{32}OSi_4$: C, 47.30; H, 10.58%.

(*Z*)-1-(2-Tetrahydropyranyloxy)-3-[tris(trimethylsilyl)silyl]-2-propene: Bp 96–100 °C (0.23 Torr, bath temp); IR (neat) 2944, 2892, 1258, 1245, 1119, 1061, 1028, 834, 686, 620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 27H), 1.48–1.92 (m, 6H), 3.47–3.54 (m, 1H), 3.84–3.92 (m, 1H), 3.97 (ddd, *J*=12.1, 7.0, 1.3 Hz, 1H), 4.28 (ddd, *J*=12.1, 5.6, 1.5 Hz, 1H), 4.64 (dd, *J*=3.9, 3.1 Hz, 1H), 5.77 (ddd, *J*=13.5, 1.5, 1.3 Hz, 1H), 6.54 (ddd, *J*=13.5, 7.0, 5.6 Hz, 1H); ^{13}C NMR ($CDCl_3$)

δ 0.93, 19.47, 25.47, 30.67, 62.17, 69.46, 98.47, 124.20, 144.72; MS (20 eV) *m/z* (rel intensity) 231 (M^+-C_5H_8O-$SiMe_3$, 18), 215 (14), 199 (6), 157 (5), 147 (6), 141 (6), 133 (8), 131 (10), 117 (9), 85 (100). Found: C, 52.40; H, 10.62%. Calcd for $C_{17}H_{40}O_2Si_4$: C, 52.51; H, 10.37%.

(*E*)-1-(2-Tetrahydropyranyloxy)-3-[tris(trimethylsilyl)silyl]-2-propene: Bp 97–101 °C (0.39 Torr, bath temp); IR (neat) 2944, 2890, 1245, 1120, 1078, 1025, 867, 831, 686, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 27H), 1.48–1.92 (m, 6H), 3.45–3.53 (m, 1H), 3.85–3.93 (m, 1H), 4.05 (ddd, *J*=13.2, 6.1, 1.3 Hz, 1H), 4.22 (ddd, *J*=13.2, 4.6, 1.5 Hz, 1H), 4.62 (dd, *J*=4.2, 2.8 Hz, 1H), 5.84 (ddd, *J*=18.4, 1.5, 1.3 Hz, 1H), 6.08 (ddd, *J*=18.4, 6.1, 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.77, 19.63, 25.49, 30.59, 62.39, 70.27, 97.23, 124.85, 143.86; MS (20 eV) *m/z* (rel intensity) 215 (M^+-C_5H_8O-$SiMe_3$, 10), 199 (11), 191 (15), 175 (11), 147 (18), 141 (13), 133 (22), 131 (24), 117 (21), 85 (94), 73 (100). Found: C, 52.71; H, 10.64%. Calcd for $C_{17}H_{40}O_2Si_4$: C, 52.51; H, 10.37%.

(*Z*)-4-[Tris(trimethylsilyl)silyl]-3-buten-1-ol: Bp 86–90 °C (0.24 Torr, bath temp); IR (neat) 3310 (bs), 2946, 2890, 1244, 1047, 833, 686, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 27H), 1.45 (bs, 1H), 2.39 (dtd, *J*=7.1, 6.6, 1.4 Hz, 2H), 3.71 (t, *J*=6.6 Hz, 2H), 5.71 (dt, *J*=13.1, 1.4 Hz, 1H), 6.40 (dt, *J*=13.1, 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.09, 38.49, 62.31, 124.32, 144.16; MS (20 eV) *m/z* (rel intensity) 247 (M^++2-$SiMe_3$, 2.5), 246 (M^++1-$SiMe_3$, 4.8), 245 (M^+-$SiMe_3$, 18), 229 (32), 201 (20), 191 (21), 175 (27), 133 (26), 131 (37), 117 (27), 73 (100). Found: C, 48.79; H, 10.96%. Calcd for $C_{13}H_{34}OSi_4$: C, 48.99; H, 10.75%.

(*E*)-4-[Tris(trimethylsilyl)silyl]-3-buten-1-ol: Bp 92–96 °C (0.30 Torr, bath temp); IR ($CDCl_3$) 3618, 2946, 2890, 1245, 1044, 982, 837, 687, 623 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 27H), 1.48 (bs, 1H), 2.40 (dtd, *J*=6.7, 6.4, 1.2 Hz, 2H), 3.64 (t, *J*=6.4 Hz, 2H), 5.70 (dt, *J*=18.2, 1.2 Hz, 1H), 5.96 (dt, *J*=18.2, 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.76, 40.93, 61.68, 125.91, 144.19; MS (20 eV)

m/z (rel intensity) 318 (M^+, 0.4), 201 (16), 191 (55), 175 (44), 155 (17), 133 (26), 131 (49), 117 (27), 73 (100). Found: C, 49.22; H, 10.82%. Calcd for $C_{13}H_{34}OSi_4$: C, 48.99; H, 10.75%.

AIBN Induced Hydrosilylation of 1-Dodecyne with $(Me_3Si)_3SiH$. A solution of 1-dodecyne (0.166 g, 1.00 mmol), $(Me_3Si)_3SiH$ (0.273 g, 1.10 mmol), and AIBN (0.016 g, 0.10 mmol) in benzene (2 mL) was refluxed for 30 min. The reaction mixture was concentrated *in vacuo*, followed by purification by silica-gel column to give 1-[tris(trimethylsilyl)silyl]-1-dodecene (0.407 g, 98%, *Z*/*E* = 4/1).

General Procedure for Isomerization of (*Z*)-Alkenylsilane to (*E*)-Isomer. Et_3B (0.96 M hexane solution, 0.52 mL, 0.50 mmol) was added to a benzene (5.0 mL) solution of (*Z*)-rich alkenylsilane (1.00 mmol) and Ph_3GeH (0.152 g, 0.500 mmol), and the resulting mixture was heated at 60 °C under argon atmosphere. After stirring for 12-16 h, the reaction mixture was concentrared *in vacuo*. Purification by silica-gel column afforded (*E*)-rich alkenylsilane.

Hydrodesilylation of 1-[tris(trimethylsilyl)silyl]-1-dodecene. Concd HCl (ca. 36%, 0.35 mL) was addded to a solution of 1-[tris(trimethylsilyl)silyl]-1-dodecene (0.415 g, 1.00 mmol) in acetonitrile (5.0 mL) and the mixture was heated at reflux. After stirring for 2 h, the reaction mixture was cooled to room temperature, and aqueous NaOH (1.0 M, 10 mL) was poured. The mixture was stirred for 1 h, then extracted with hexane (20 mL x 3). Concentration of the dried (Na_2SO_4) organic layer and purification by silica-gel column gave 1-dodecene (0.161 g) in 96% yield. The use of Me_3SiCl (0.50 mL, 4.0 mmol) and D_2O (0.072 mL, 4.0 mmol) instead of concd HCl afforded 1-deuterio-1-dodecene (0.152 g, 90% D, *Z*/*E* > 20/1) in 90% yield. Hydrodesilylation of (*Z*)-1-deuterio-1-[tris(trimethylsilyl)silyl]-1-dodecene was performed according to the same procedure as above.

Bromodesilylation of 1-[tris(trimethylsilyl)silyl]-1-dodecene.

Bromine (1.0 M CH_2Cl_2 solution, 2.0 mL, 2.0 mmol) was added dropwise to a solution of 1-[tris(trimethylsilyl)silyl]-1-dodecene (0.207 g, 0.500 mmol) in CH_2Cl_2 at -25 °C. After stirring for 30 min, the reaction mixture was treated with aqueous $Na_2S_2O_5$ (10 %, 2.0 mL), and immediately warmed to room temperature. The resulting mixture was poured into water (20 mL) , and extracted with Et_2O (20 ml x 2). The combined organic layer was dried over Na_2SO_4, then concentrated *in vacuo*. The crude product was treated with silica-gel (1.0 g) in hexane (5 ml) for 2 h at room temperature. After filtration of the mixture through Na_2SO_4 column, the filtrate was concentrated *in vacuo*. The residual oil was purified by silica-gel column (hexane) to give 1-bromo-1-dodecene in 83% yield (0.103 g, *Z*/*E* = 2.3/1).

General Procedure for Reduction of Alkenyl Iodide with $(Me_3Si)_3SiH$-Et_3B or *n*-Bu_3SnH-Et_3B. Et_3B (0.96 M, 0.10 mL, 0.10 mmol) was added to a benzene (2.0 mL) solution of alkenyl iodide (1.00 mmol) and $(Me_3Si)_3SiH$ (0.274 g, 1.10 mmol) at room temperature under argon atmosphere. The mixture was stirred for 2 h, followed by an addititon of aqueous NaOH (1.0 M, 10 mL). After stirring for another 2 h, the resultant mixture was extracted with hexane (10 mL x 3). Combined organic layers were dried over Na_2SO_4, and concentrated *in vacuo*. The residual oil was purified by silica-gel column.

The reaction conditions for reduction with *n*-Bu_3SnH was similar to with $(Me_3Si)_3SiH$. The work-up procedure is as follows. After stirring for 2 h, the reaction mixture was concentrated *in vacuo*, and the residue was dissolved in CH_2Cl_2 (10 mL). Anhydrous KF (1.0 g) and saturated aqueous KF (2.0 mL) was added to the CH_2Cl_2 solution. After stirring for several hours, resulting precipitate was filtered through Na_2SO_4, and the filtrate was concentrated *in vacuo*. After the residue was dissolved in hexane (1.0 mL), the solution was submitted to silica-gel column.

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CHAPTER 6

Tris(trimethylsilyl)silyl Radical Induced Bicyclization of 1,6-Dienes and 1,6-Enynes Providing 3,3-Bis(trimethylsilyl)-3-silabicyclo[3.3.0]octanes and 3-Silabicyclo[3.3.0]oct-1-enes

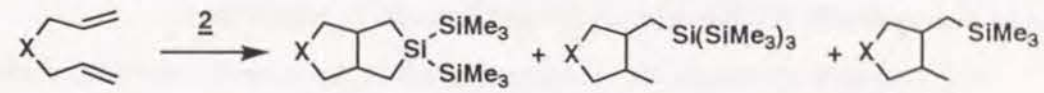
Treatment of 1,6-dienes with tris(trimethylsilyl)silane in the presence of Et_3B or AIBN afforded 3,3-bis(trimethylsilyl)-3-silabicyclo[3.3.0]octanes in addition to monocyclized cyclopentanes. Bicyclization of 1,6-enynes provided the corresponding 3-silabicyclo[3.3.0]oct-1-enes.

The formation of carbocyclic and heterocyclic compounds from diene[1] or enyne[2] by free-radical processes has received considerable attention in recent years.[3] We have reported that Et_3B induced a radical cyclization of enyne by the use of triphenylstannane[2a] or triphenygermane[2b] under mild condition. Recently, tris(trimethylsilyl)silane (TTMSS) as an alternative to tributylstannane has become more popular, being a superior reagent from both ecological and practical perspectives. This silane can be used as a reducing agent for organic compounds or a hydrosilylating agent for alkenes and alkynes.[4, 5] Then, we examined Et_3B induced radical cyclization of diene and enyne mediated by TTMSS. To our surprise, the radical reaction gave a silabicyclic compound along with expected cyclopentane derivatives. Here, we present an efficient method for the preparation of bicycles such as 3,3-bis(trimethylsilyl)-3-silabicyclo[3.3.0]octane or 3,3-bis(trimethylsilyl)-3-silabicyclo[3.3.0]oct-1-ene based on the tandem radical cyclization of diene or enyne promoted by tris(trimethylsilyl)silyl radical.[6] In addition, a recent publication[7] on homolytic substitution reaction at a silicon atom prompts us to report our independent results[8] along similar lines.

(1) The Reaction of Diene with TTMSS. When a benzene solution of diene **1a** and TTMSS (**2**) was treated at room temperature with a catalytic amount of Et_3B (Method A), bicyclized product **3a** (11%) was obtained along with monocyclized product **4a** (87%).[9] In an effort to increase both the yield and the ratio of **3a** to **4a**, the reaction was repeated under various reaction conditions. The yields of **3a** and **4a** were 71% and 17%, respectively, and the ratio **3a**/**4a** had increased to 81/19 upon treatment of **1a** (1.00 mmol) with **2** (1.30 mmol) at 80 °C using an initial concentration of **1a** of 0.02 M with intermittent addition of AIBN (0.10 mmol x 5) over 5 h (Method B). Under these reaction conditions monocyclized product **4a** was *trans*-rich (*trans*-**4a**/*cis*-**4a** = 2/1), and trimethylsilyl-

methyl-substituted cyclopentane **5a** was obtained in 8% yield in addition to the formation of **3a** and **4a** (Table 1).

Table 1. The Reaction of Dienes with TTMSS[a]

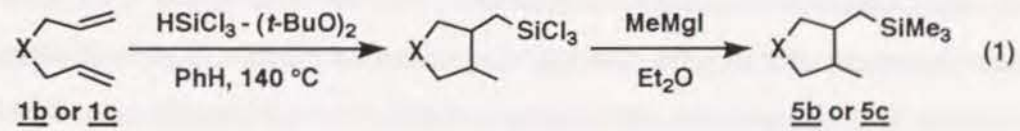


1 **3** **4** **5**

	X	Yield/% (*cis*/*trans*)[b]		
		3	**4**	**5**
1a:	$C(COOMe)_2$	71 (15/1)	17 (1/2)	8 (5/1)
1b:	CH_2	62 (6/1)	27 (1/5)	4 (3/1)
1c:	O	53 (cis only)	26 (1/8)	3 (3/1)

a) Diene (1.00 mmol), TTMSS (1.30 mmol), AIBN (0.10 mmol x 5) and benzene (50 mL) were employed (Method B). b) Yields and isomeric ratios were determined by the examination of ^1H NMR of the mixture of **3**, **4**, and **5** after purification.

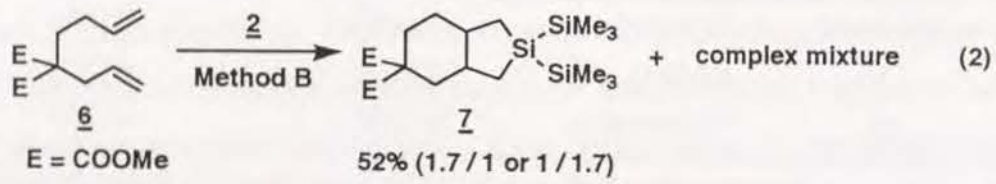
In a similar manner, dienes **1b** and **1c** were converted into the corresponding bicyclized products **3b** and **3c**. Two types of monocyclized products **4** and **5** were also obtained as a mixture of *cis* and *trans* compounds.[10] Trimethylsilylmethyl-substituted cyclopentane **5b** and tetrahydrofuran **5c** were synthesized independently by an another procedure to prove the structure of these compounds (eq 1).[11]



1b or **1c** **5b** or **5c** (1)

Whereas **3c** was produced in an isomerically pure form (*cis*-fused compound), **3a** and **3b** were obtained as isomeric mixtures of *cis*-fused and *trans*-fused 3-silabicyclooctanes.[12] Formation of a negligible amount of highly strained *trans*-**3c** is predicted by calculations on MacroModel[13], which indicate that *cis*-**3c** is about 2.4 kcal/mol more stable than *trans*-**3c**. Meantime, the calculations show that an energy difference between *cis*-**3b** and *trans*-**3b** is 1.2 kcal/mol.

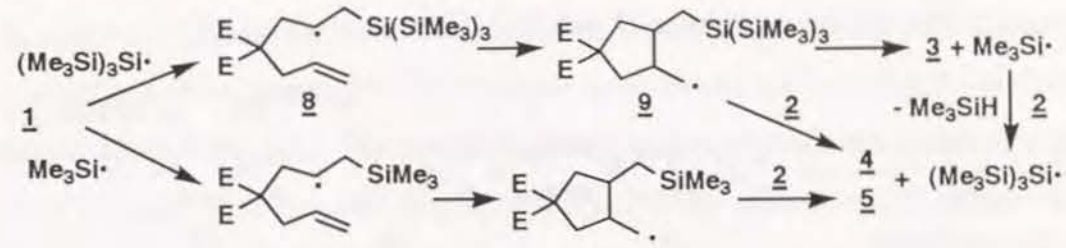
A 1,7-diene **6** afforded a bicyclized product **7** as the isomeric mixture of *cis*- and *trans*-fused compounds in 52% yield. The stereoselectivity of **7** was low and the ratio of two isomers was 1.7/1 (eq 2).



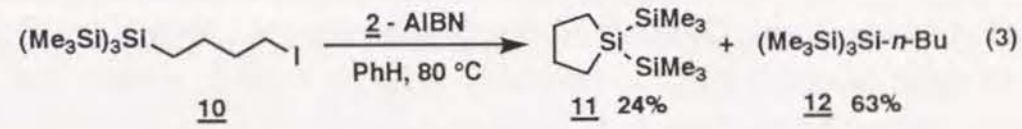
These results support the following reaction mechanism for bicyclization of dienes (Scheme 1). The tris(trimethylsilyl)silyl radical, generated by the action of radical initiator on **2**, attacks terminal olefinic carbon of 1,6-diene to give a carbon radical **8**, which cyclizes to cyclopentylmethyl radical **9**. The carbon radical attacks silicon having three trimethylsilyl groups to produce **3** under elimination of trimethylsilyl radical. Trimethylsilyl radical abstracts hydrogen of **2**, and regenerates tris(trimethylsilyl)silyl radical.

In the homolytic substitution, *cis*-**9** reacts much faster than *trans*-**9** to provide **3** because of facile approach of the radical center to tris(trimethylsilyl)silyl group. Meantime, the intramolecular reaction of *trans*-**9** is slow, and this radical abstracts hydrogen of **2** to give monocyclized product **4** predominantly. For this reason, Method B affords *trans*-rich cyclopentane **4**. Moreover, the formation of **5** certifies the intermediacy of trimethylsilyl radical.

Scheme 1.



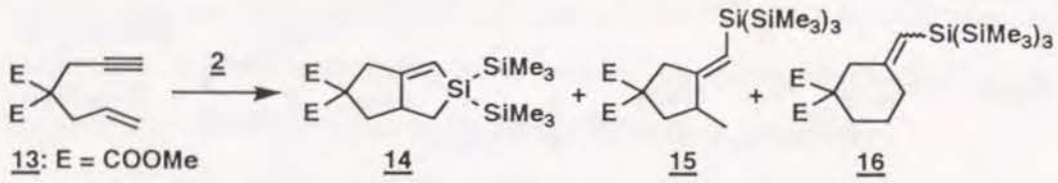
The Si-Si bond fission by the intramolecular attack of carbon radical was confirmed by the experiment shown below (eq 3). Treatment of iodoalkylsilane **10** with **2** gave silacyclopentane **11** in 24% yield along with the reduced product **12** (63%).



(2) The Reaction of Enyne with TTMSS. In order to demonstrate the applicability of this bicyclization, the reaction of 1,6-enyne with **2** has been examined. Treatment of a hexane (2 mL) solution of enyne **13** (1.00 mmol) and **2** (1.30 mmol) with Et_3B (0.10 mmol) (Method A') gave 3-silabicyclo[3.3.0]oct-1-ene **14** (53%) as a major product in addition to methylenecyclopentane **15** (17%) and methylenecyclohexane **16** (20%). The change of radical initiator and concentration of enyne **13** was not effective for increase of the yield of **14** (Table 2).

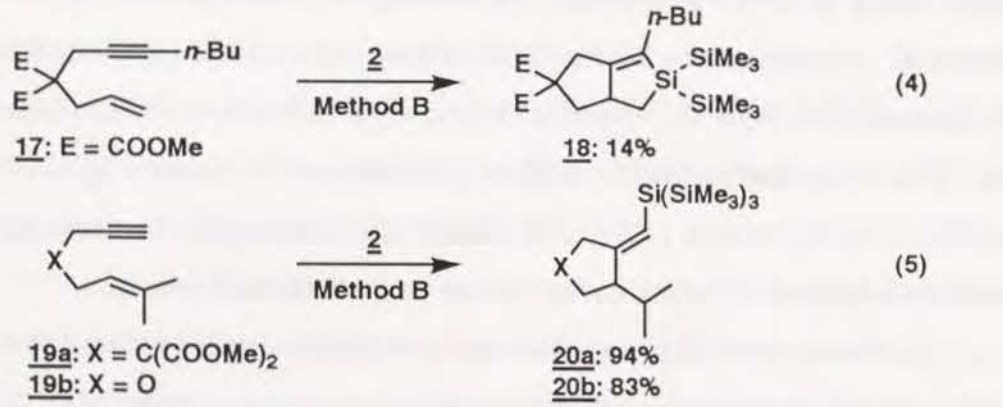
The use of enyne **17** provided the corresponding bicyclized product **18** in only 14% yield along with unidentified complex products even under high dilution condition (eq 4). In the case of enynes **19a** and **19b**, methylenecyclopentane **20a** (94%) and **20b** (83%) formed and no trace of bicyclized products was detected in the reaction mixture (eq 5).

Table 2. The Reaction of Enyne **13** with TTMSS[a)]



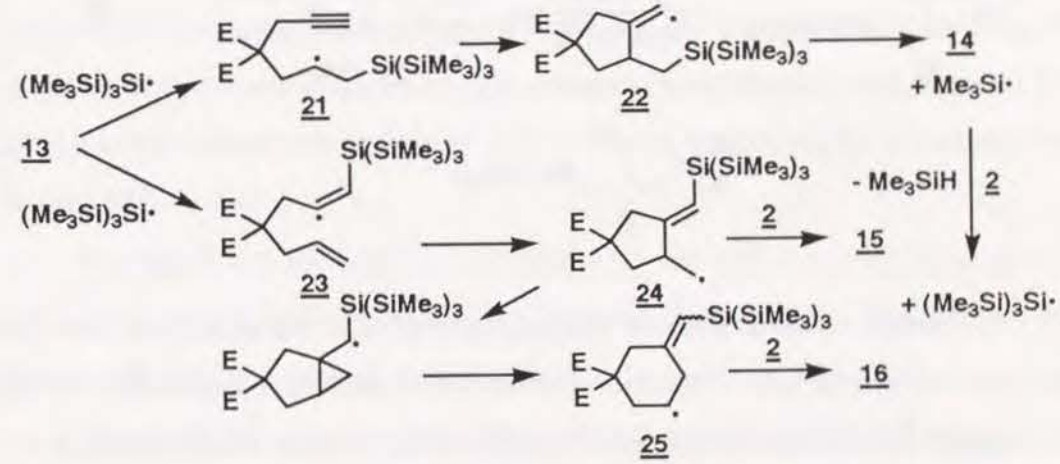
Method	Yield/%		
	14	**15**	**16**
A'	53	17	20
C	47	5	36
B	50	<1	38

a) **13** (1.00 mmol) and TTMSS (1.30 mmol) were employed. Method A' : Et_3B (0.10 mmol), hexane (2 mL), r.t.; Method C : AIBN (0.10 mmol), benzene (5 mL), reflux; Method B : See Table 1. b) Yields were determined by the examination of ^1H NMR.



Based on these facts we assume the following reaction mechanism for the reaction of enyne **13** with **2** (Scheme 2). Tris(trimethylsilyl)silyl radical, given by the reaction of **2** with radical initiator, can attack either terminal olefinic carbon or terminal acetylenic carbon.[14)] The attack on terminal olefinic carbon gives olefinic radical **22** *via* radical **21**. Intramolecular homolytic substitution of **22** affords **14** accompanying with the elimination of trimethylsilyl radical, which regenerate tris(trimethylsilyl)silyl radical by the abstraction of hydrogen from **2**. On the other hand, an addition of tris(trimethylsilyl)silyl radical to terminal acetylenic carbon provides alkenyl radical **23**. The intramolecular addition of carbon radical to double bond in **23** proceeds on the opposite side of tris(trimethylsilyl)silyl group to avoid the steric hindrance, and gives cyclopentylmethyl radical **24** with (*E*)-stereochemistry.[2a)] Therefore, **24** can not afford **14** because of its geometry, and abstracts hydrogen from **2** to provide **15**. Alternatively, **24** rearranges to cyclohexyl radical **25** which reacts with **2** to give **16**.[15)]

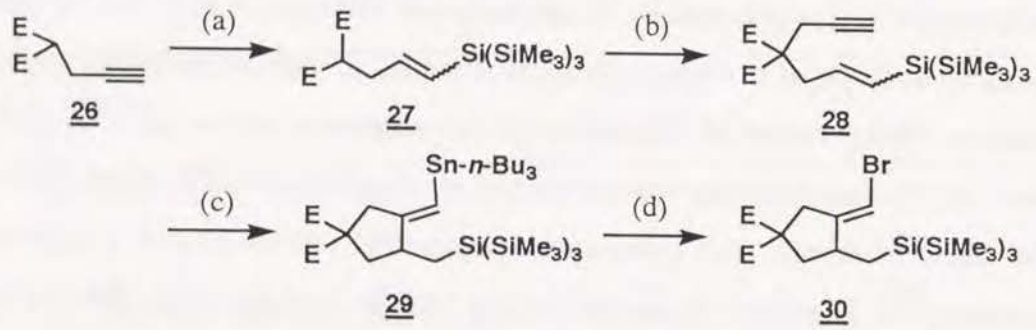
Scheme 2.



To confirm this mechanism, alkenyl bromide **30** was synthesized from **26** as shown in Scheme 3. Treatment of **30** with **2** in the presence of AIBN gave **14** in

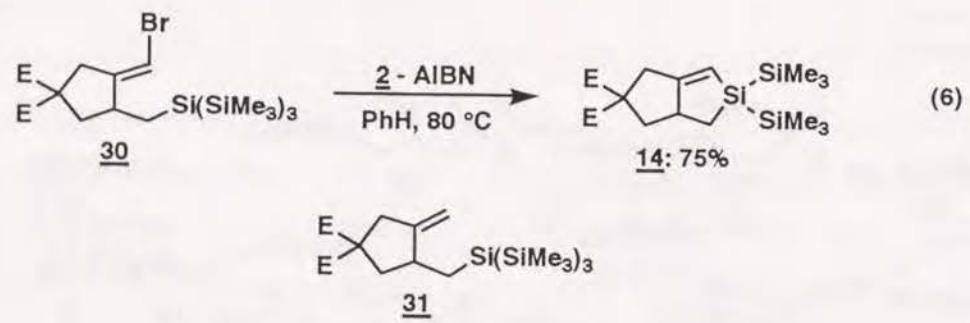
good yield, and this result supports the homolytic substitution of **22** (eq 6). The reduced product **31** could not be observed in the reaction mixture. Thus, the intramolecular cyclization of **22** was much faster than an abstraction of hydrogen from **2**.

Scheme 3.



26 27 28 29 30

(a) **2**, AIBN, benzene, reflux, 2 h. (b) NaH, THF, r.t., 30 min, then propargyl bromide, r.t., 4 h. (c) n-Bu_3SnH, AIBN, benzene, reflux, 2 h. (d) Br_2, CH_2Cl_2, -78 °C, 25 min.



In conclusion, the addition of tris(trimethylsilyl)silyl radical to diene or enyne provides us with a new synthetic method for silabicyclo compounds. To our knowledge, this reaction is the first example of the reaction which proceeds *via* homolytic substitution at silicon by carbon radical.[7,16]

Experimental

General Procedure for the Reaction of Diene or Enyne with TTMSS.

Method A: Typical procedure is as follows. Et_3B (0.96 M hexane solution, 0.10 mL, 0.10 mmol) was added to a benzene (5 mL) solution of diene **1a** (0.212 mg, 1.00 mmol) and TTMSS (0.323 mg, 1.30 mmol) at room temperature under argon atmosphere. After stirring for 1.3 h, the reaction mixture was concentrated *in vacuo*. The residual oil was purified by silica-gel column chromatography (hexane/AcOEt = 20/1) to give a mixture of bicyclized product **3a** and monocyclized product **4a**. The yield and the diastereomeric ratio of **3a** or **4a** were determined by the examination of ^1H NMR.

Method A': In Method A, hexane is used as a solvent instead of benzene.

Method B: A benzene solution of diene **1** (1.00 mmol) and TTMSS (0.323 mg, 1.30 mmol) was stirred and heated at reflux under argon atmosphere. AIBN (0.10 M benzene solution, 1.0 mL, 0.10 mmol) was added to the mixture five times at intervals of 1 h. After the last addition of AIBN followed by stirring for 1 h, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The crude product was purified by silica-gel column to give a mixture of **3**, **4** and **5**. The yield and the diastereomeric ratio of **3**, **4** or **5** were determined by the examination of ^1H NMR.

Method C: AIBN (0.016 g, 0.10 mmol) was added to a benzene (5 mL) solution of enyne (1.00 mmol) and **2** (0.323 mg, 1.30 mmol). The mixture was heated at reflux for 2.5 h with stirring. Work-up is similar to Method B.

Dimethyl *cis*-3,3-Bis(trimethylsilyl)-3-silabicyclo[3.3.0]octane-7,7-dicarboxylate (*cis*-3a): Bp 101–105 °C (0.28 Torr, bath temp); IR (neat) 2946, 1736, 1259, 1246, 1195, 1154, 834, 687, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.09 (s, 9H), 0.13 (s, 9H), 0.71 (dd, J=14.9, 5.6 Hz, 2H), 1.01 (dd, J=14.9, 7.1 Hz, 2H),

1.95–2.05 (m, 2H), 2.38–2.49 (m, 4H), 3.71 (s, 6H); ^{13}C NMR ($CDCl_3$) δ -0.93, -0.74, 12.57, 41.30, 46.20, 52.69 (two carbons), 60.06, 173.48; MS (20 eV) *m/z* (rel intensity) 372 (M^++1-Me, 0.8), 371 (M^+-Me, 3.2), 355 (1.6), 316 (M^++3-$SiMe_3$, 1.8), 315 (M^++2-$SiMe_3$, 12), 314 (M^++1-$SiMe_3$, 22), 313 (M^+-$SiMe_3$, 100), 163 (23). Found: C, 52.73; H, 9.13%. Calcd for $C_{17}H_{34}O_4Si_3$: C, 52.80; H, 8.86%.

Dimethyl *trans*-3,3-Bis(trimethylsilyl)-3-silabicyclo[3.3.0]octane-7,7-dicarboxylate (*trans*-3a): Bp 97–101 °C (0.27 Torr, bath temp); IR ($CHCl_3$) 2948, 2888, 1727, 1245, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 18H), 0.39–0.49 (m, 2H), 0.90–0.98 (m, 2H), 1.50–1.63 (m, 4H), 2.51–2.56 (m, 2H), 3.72 (s, 6H); ^{13}C NMR ($CDCl_3$) δ -0.91, 10.73, 39.90, 52.63, 52.99, 63.16, 173.42; MS (70 eV) *m/z* (rel intensity) 387 (M^++1, 5.5), 386 (M^+, 7.4), 314 (M^++1-$SiMe_3$, 4.3), 313 (M^+-$SiMe_3$, 17), 133 (14), 113 (14), 73 (100). Found: C, 52.53; H, 9.15%. Calcd for $C_{17}H_{34}O_4Si_3$: C, 52.80; H, 8.86%.

Dimethyl *cis*-4-Methyl-3-{[tris(trimethylsilyl)silyl]methyl}cyclopentane-1,1-dicarboxylate (*cis*-4a): Bp 107–111 °C (0.26 Torr, bath temp); IR (neat) 2948, 2890, 1735, 1435, 1246, 1199, 1149, 834, 684, 622 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 27H), 0.64 (dd, *J*=14.3, 9.5 Hz, 1H), 0.85 (d, *J*=6.8 Hz, 3H), 0.93 (dd, *J*=14.3, 3.5 Hz, 1H), 1.94 (dd, *J*=12.8, 9.3 Hz, 1H), 1.98 (dd, *J*=13.5, 4.9 Hz, 1H), 2.00–2.15 (m, 2H), 2.41 (dd, *J*=12.8, 6.3 Hz, 1H), 2.42 (dd, *J*=13.5, 6.6 Hz, 1H), 3.70 (s, 3H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 1.25, 7.37, 14.81, 37.91, 40.93, 41.15, 42.04, 52.64 (two carbons), 58.77, 173.32, 173.47; MS (20 eV) *m/z* (rel intensity) 446 (M^++1-Me, 2.3), 445 (M^+-Me, 3.4), 389 (M^++2-$SiMe_3$, 13), 388 (M^++1-$SiMe_3$, 31), 387 (M^+-$SiMe_3$, 88), 207 (15), 206 (19), 205 (100), 175 (14), 173 (15). Found: C, 52.11; H, 9.88%. Calcd for $C_{20}H_{44}O_4Si_4$: C, 52.12; H, 9.62%.

Dimethyl *trans*-4-Methyl-3-{[tris(trimethylsilyl)silyl]methyl}cyclo-

pentane-1,1-dicarboxylate (*trans*-4a): Bp 105–109 °C (0.23 Torr, bath temp); IR (neat) 2948, 2890, 1737, 1435, 1246, 1169, 1144, 834, 684, 622 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 27H), 0.49 (dd, *J*=14.3, 11.0 Hz, 1H), 0.99 (d, *J*=6.1 Hz, 3H), 1.21 (dd, *J*=14.3, 2.4 Hz, 1H), 1.33–1.56 (m, 2H), 1.71 (dd, *J*=13.2, 11.0 Hz, 1H), 1.79 (dd, *J*=13.6, 10.7 Hz, 1H), 2.47 (dd, *J*=13.6, 7.0 Hz, 1H), 2.60 (dd, *J*=13.2, 6.4 Hz, 1H), 3.71 (s, 3H), 3.72 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 1.26, 11.00, 17.44, 42.29, 43.55, 43.76, 46.63, 52.60 (two carbons), 57.94, 173.27, 173.36; MS (20 eV) *m/z* (rel intensity) 446 (M^++1-Me, 2.1), 445 (M^+-Me, 4.5), 389 (M^++2-$SiMe_3$, 11), 388 (M^++1-$SiMe_3$, 26), 387 (M^+-$SiMe_3$, 79), 207 (12), 206 (18), 205 (100), 175(13). Found: C, 51.92; H, 9.61%. Calcd for $C_{20}H_{44}O_4Si_4$: C, 52.12; H, 9.62%.

Dimethyl *cis*-4-Methyl-3-[(trimethylsilyl)methyl]cyclopentane-1,1-dicarboxylate (*cis*-5a): Bp 66–70 °C (0.31 Torr, bath temp); IR (neat) 2950, 2900, 1735, 1435, 1250, 1219, 1202, 1151, 858, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9H), 0.46 (dd, *J*=14.6, 9.1 Hz, 1H), 0.58 (dd, *J*=14.6, 5.0 Hz, 1H), 0.82 (d, *J*=6.6 Hz, 3H), 1.89 (dd, *J*=13.3, 3.7 Hz, 1H), 2.02–2.13 (m, 3H), 2.33–2.40 (m, 2H), 3.72 (s, 6H); ^{13}C NMR ($CDCl_3$) δ -0.87, 14.87, 16.64, 37.69, 39.02, 40.64, 41.21, 52.65 (two carbons), 58.85, 173.47, 173.66; MS (20 eV) *m/z* (rel intensity) 286 (M^+, 0.7), 272 (M^++1-Me, 5.6), 271 (M^+-Me, 25), 229 (12), 185 (14), 151 (13), 145 (100), 140 (10), 113 (15), 108 (31), 73 (53). Found: C, 58.47; H, 9.35%. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15%.

Dimethyl *trans*-4-Methyl-3-[(trimethylsilyl)methyl]cyclopentane-1,1-dicarboxylate (*trans*-5a): Bp 68–72 °C (0.30 Torr, bath temp); IR (neat) 2950, 1736, 1436, 1251, 1212, 1195, 1171, 1144, 858, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9H), 0.29 (dd, *J*=14.5, 10.8 Hz, 1H), 0.86 (dd, *J*=14.5, 2.4 Hz, 1H), 0.95 (d, *J*=6.1 Hz, 3H), 1.34–1.55 (m, 2H), 1.65 (d, *J*=13.2 Hz, 1H), 1.68 (d, *J*=13.4 Hz, 1H), 2.52 (dd, *J*=13.2, 6.6 Hz, 1H), 2.58 (dd, *J*=13.4, 6.5 Hz, 1H), 3.72 (s,

6H); ^{13}C NMR ($CDCl_3$) δ -0.86, 17.15, 20.21, 42.15, 42.69, 43.50, 43.55, 52.64 (two carbons), 58.11, 173.48 (two carbons); MS (20 eV) *m/z* (rel intensity) 286 (M^+, 1.1), 272 (M^++1-Me, 4.3), 271 (M^+-Me, 25), 217 (16), 146 (15), 145 (100), 113 (27), 108 (31), 89 (55), 73 (85). Found: C, 58.57; H, 9.45%. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15%.

***cis*-3,3-Bis(trimethylsilyl)-3-silabicyclo[3.3.0]octane (*cis*-3b):** Bp 55–59 °C (0.33 Torr, bath temp); IR (neat) 2944, 2894, 2866, 1243, 832, 686, 621 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9H), 0.12 (s, 9H), 0.66 (dd, *J*=14.6, 6.3 Hz, 2H), 0.97 (dd, *J*=14.6, 8.1 Hz, 2H), 1.22–1.35 (m, 2H), 1.44–1.61 (m, 1H), 1.65–1.81 (m, 3H), 2.22–2.35 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -0.80, -0.60, 13.28, 23.50, 33.32, 46.66; MS (70 eV) *m/z* (rel intensity) 272 (M^++2, 3.0), 271 (M^++1, 4.5), 270 (M^+, 14), 197 (M^+-$SiMe_3$, 35), 169 (11), 137 (22), 117 (25), 103 (18), 73 (76), 40 (100). Found: C, 57.72; H, 10.89%. Calcd for $C_{13}H_{30}Si_3$: C, 57.69; H, 11.17%.

***trans*-3,3-Bis(trimethylsilyl)-3-silabicyclo[3.3.0]octane (*trans*-3b):** Bp 62–66 °C (0.44 Torr, bath temp); 2946, 2888, 2858, 1244, 833, 778, 688, 620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 18H), 0.40 (dd, *J*=13.4, 12.1 Hz, 2H), 0.91 (dd, *J*=13.4, 5.6 Hz, 2H), 0.99–1.13 (m, 2H), 1.34–1.51 (m, 2H), 1.67–1.77 (m, 2H), 1.86–1.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -0.86, 11.15, 27.48, 31.05, 54.39; MS (70 eV) *m/z* (rel intensity) 272 (M^++2, 4.4), 271 (M^++1, 8.2), 270 (M^+, 24), 197 (M^+-$SiMe_3$, 24), 182 (10), 137 (34), 136 (15), 123 (10), 122 (11), 117 (33), 103 (24), 73 (100). Found: C, 57.53; H, 11.40%. Calcd for $C_{13}H_{30}Si_3$: C, 57.69; H, 11.17%.

2-Methyl-1-[(trimethylsilyl)methyl]cyclopentane (5b, *cis*/*trans* = 3/1): Bp 70–74 °C (43 Torr, bath temp); IR (neat) 2948, 2896, 2864, 1248, 860, 836, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.01 (s, 9H), 0.27 (dd, *J*=14.3, 10.4 Hz, 0.25H), 0.42 (dd, *J*=14.5, 9.5 Hz, 0.75H), 0.59 (dd, *J*=14.5, 4.7 Hz, 0.75H), 0.77 (d, *J*=6.8 Hz, 2.25H), 0.85 (dd, *J*=14.3, 2.9 Hz, 0.25H), 0.93 (d, *J*=6.2 Hz, 0.75H), 1.02–1.34 (m,

3H), 1.43–1.95 (m, 5H); ^{13}C NMR ($CDCl_3$), *cis* isomer δ -0.79, 14.81, 17.41, 22.50, 32.08, 32.98, 38.12, 39.33, *trans* isomer δ -0.79, 18.47, 21.49, 23.06, 33.96, 34.62, 44.11, 44.29; MS (70 eV) *m/z* (rel intensity) 171 (M^++1, 0.2), 170 (M^+, 1.5), 156 (M^++1-Me, 1.3), 155 (M^+-Me, 8.1), 73 (100). Found: C, 70.64; H, 13.29%. Calcd for $C_{10}H_{22}Si$: C, 70.50; H, 13.02%.

***cis*-7,7-Bis(trimethylsilyl)-3-oxa-7-silabicyclo[3.3.0]octane (*cis*-3c):** Bp 71–74 °C (0.78 Torr, bath temp); IR (neat) 2944, 2890, 2848, 1244, 1068, 833, 773, 688, 621 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9H), 0.13 (s, 9H), 0.76 (dd, *J*=14.8, 6.2 Hz, 2H), 1.04 (dd, *J*=14.8, 8.0 Hz, 2H), 2.57–2.70 (m, 2H), 3.43 (dd, *J*=8.2, 5.4 Hz, 2H), 3.93 (dd, *J*=8.2, 6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ -0.92, -0.75, 10.54, 46.25, 74.64; MS (70 eV) *m/z* (rel intensity) 273 (M^++1, 0.3), 272 (M^+, 0.6), 258 (M^++1-Me, 0.3), 257 (M^+-Me, 1.0), 189 (19), 157 (18), 143 (13), 131 (23), 117 (20), 73 (100). Found: C, 52.57; H, 10.55%. Calcd for $C_{12}H_{28}OSi_3$: C, 52.87; H, 10.35%.

***cis*-4-Methyl-3-[(trimethylsilyl)methyl]tetrahydrofuran (*cis*-5c):** Bp 87–91°C (29 Torr, bath temp); IR (neat) 2952, 2916, 2852, 1249, 1062, 1031, 910, 860, 839, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9H), 0.48 (dd, *J*=14.7, 9.5 Hz, 1H), 0.64 (dd, *J*=14.7, 5.4 Hz, 1H), 0.91 (d, *J*=7.0 Hz, 3H), 2.12–2.35 (m, 2H), 3.31 (dd, *J*=8.7, 8.0 Hz, 1H), 3.49 (dd, *J*=8.1, 3.4 Hz, 1H), 3.89 (dd, *J*=8.1, 2.4 Hz, 1H), 3.91 (dd, *J*=8.0, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.02, 13.19, 13.89, 37.32, 38.48, 73.30, 75.08; MS (20 eV) *m/z* (rel intensity) 158 (M^++1-Me, 1.1), 157 (M^+-Me, 7.9), 130 (7.2), 129 (13), 116 (8), 115 (80), 103 (12), 73 (100). Found: C, 62.67; H, 11.93%. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70%.

***trans*-4-Methyl-3-[(trimethylsilyl)methyl]tetrahydrofuran (*trans*-5c):** Bp 88–92 °C (30 Torr, bath temp); IR (neat) 2952, 2918, 2892, 2866, 1249, 1044, 925, 859, 839, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 0.38 (dd, *J*=14.6, 10.4 Hz, 1H), 0.88 (dd, *J*=14.6, 3.4 Hz, 1H), 0.99 (d, *J*=6.4 Hz, 3H), 1.62–1.83 (m, 2H),

3.27 (t, *J*=8.1 Hz, 1H), 3.30 (t, *J*=8.0 Hz, 1H), 3.97 (dd, *J*=8.1, 7.2 Hz, 1H), 4.03 (dd, *J*=8.0, 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.05, 15.26, 18.63, 43.28, 43.46, 74.67, 75.26; MS (20 eV) *m/z* (rel intensity) 158 (M^++1-Me, 1.2), 157 (M^+-Me, 10), 130 (7.0), 129 (12), 116 (5), 115 (47), 103 (15), 73 (100). Found: C, 62.78; H, 11.88%. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70%.

Synthesis of 5b and 5c by hydrosilylation of 1,6-heptadiene or diallyl ether with Cl_3SiH. Preparation of **5c** is representative. A benzene (20 mL) solution of di-*t*-butyl peroxide (0.73 g, 5.0 mmol), diallyl ether **1c** (0.98 g, 10 mmol), and Cl_3SiH (4.1 mL, 40 mmol) was heated at 140 °C in a sealed tube under argon atmosphere. After stirring for 8 h, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residual oil was diluted with Et_2O (10 mL) under argon atmosphere. MeMgI (0.96 M Et_2O solution, 37 mL, 36 mmol) was added dropwise over 10 min to this solution at 0 °C. After addition of MeMgI, the mixture was stirred for 13 h at room temperature. The reaction mixture was poured into ice (50 g) and 1M aqueous HCl (50 mL), and extracted with Et_2O (30 mL x 2). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated, the residual oil was purified by silica-gel column (hexane/Et_2O = 10/1) to give **5c** (0.64 g, *cis*/*trans* = 1.7/1) in 37% yield. **5b** was also obtained by this procedure in 22% yield.

Dimethyl 8,8-Bis(trimethylsilyl)-8-silabicyclo[4.3.0]nonane-3,3-dicarboxylate (7, major isomer): Bp 101–105 °C (0.29 Torr, bath temp); IR (neat) 2946, 1734, 1258, 1243, 1218, 1157, 1139, 836, 777, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9H), 0.10 (s, 9H), 0.37–0.50 (m, 2H), 0.85–1.26 (m, 5H), 1,45 (dd, *J*=13.4, 11.1 Hz, 1H), 1.64 (td, *J*=13.5, 3.9 Hz, 1H), 1.93 (dm, *J*=13.1 Hz, 1H), 2.37 (dm, *J*=13.4 Hz, 1H), 2.58 (dt, *J*=13.3, 2.6 Hz, 1H), 3.70 (s, 3H), 3.73 (s, 3H); ^{13}C NMR ($CDCl_3$) δ -0.90 (two peaks), 15.41, 15.73, 32.00, 32.65, 40.83, 43.15, 46.13, 52.33, 52.61, 55.91, 171.74, 173.14; MS (70 eV) *m/z* (rel intensity)

402 (M^++2, 1.9), 401 (M^++1, 4.4), 400 (M^+, 13), 163 (14), 149 (11), 133 (14), 119 (11), 117 (13), 73 (100). Found: C, 53.76; H, 9.08%. Calcd for $C_{18}H_{36}O_4Si_3$: C, 53.95; H, 9.05%.

Dimethyl 8,8-Bis(trimethylsilyl)-8-silabicyclo[4.3.0]nonane-3,3-dicarboxylate (7, minor isomer): Bp 110–114 °C (0.40 Torr, bath temp); IR (neat) 2946, 1735, 1245, 1152, 834, 621 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9H), 0.15 (s, 9H), 0.59 (dd, *J*=14.6, 2.0 Hz, 1H), 0.68 (dd, *J*=14.5, 6.6 Hz, 1H), 0.95 (dd, *J*=14.5, 12.0 Hz, 1H), 1.05 (dd, *J*=14.6, 5.9 Hz, 1H), 1.48–2.15 (m, 8H), 3.69 (s, 3H), 3.74 (s, 3H); ^{13}C NMR ($CDCl_3$) δ -0.92, -0.41, 9.11, 14.67, 25.32, 26.59, 33.38, 37.83, 40.04, 52.33, 52.58, 55.30, 171.85, 173.07; MS (20 eV) *m/z* (rel intensity) 385 (M^+-Me, 2), 328 (M^++1-$SiMe_3$, 26), 327 (M^+-$SiMe_3$, 100), 163 (28). Found: C, 53.71; H, 9.29%. Calcd for $C_{18}H_{36}O_4Si_3$: C, 53.95; H, 9.05%.

4-[Tris(trimethylsilyl)silyl]butyl *p*-Toluenesulfonate. AIBN (0.14g, 0.85 mmol) was added to a benzene (17 mL) solution of 3-butenyl *p*-toluenesulfonate (1.93 g, 8.53 mmol) and **2** (2.85 mL, 9.38 mmol) under argon atmosphere. The mixture was heated at reflux and stirred for 3 h. The reaction did not complete, then AIBN (0.14g, 0.85 mmol) was added again. After stirring for another 2 h, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The crude product was purified by silica-gel column chromatography (hexane/AcOEt = 10/1) to give the title compound (2.32g, 57%): Mp 45.8–46.9 °C (Hexane); IR ($CDCl_3$) 2948, 1358, 1245, 1189, 1177, 927, 836, 814 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 27H), 0.65–0.71 (m, 2H), 1.33–1.44 (m, 2H), 1.63–1.72 (m, 2H), 2.45 (s, 3H), 4.03 (t, *J*=6.4 Hz, 2H), 7.32–7.36 (m, 2H), 7.77–7.81 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 1.09, 7.04, 21.64, 24.87, 32.93, 69.93, 127.84, 129.81, 133.15, 144.59; MS (20 eV) *m/z* (rel intensity) 403 (M^++2-$SiMe_3$, 11), 402 (M^++1-$SiMe_3$, 4.4), 401 (M^+-$SiMe_3$, 21), 347 (22), 346 (34), 345 (100), 287 (15). Found: C, 50.29; H, 9.13%. Calcd for $C_{20}H_{42}O_3Si_4S$: C, 50.58; H, 8.91%.

1-Iodo-4-[tris(trimethylsilyl)silyl]butane (10). A solution of 4-[tris(trimethylsilyl)silyl]butyl *p*-toluenesulfonate (2.32 g, 4.89 mmol), prepared as shown above, and NaI (2.19 g, 14.6 mmol) in acetone (15 mL) was stirred for 20 h at room temperature. Resulting white precipitate was filtered through Na_2SO_4, and the filtrate was concentrated *in vacuo*. The crude product was diluted with water (30 mL), and extracted with hexane (30 mL x 2). The combined organic layer was dried over Na_2SO_4, followed by concentration and purification by silica-gel column (hexane) to give the title compounds (1.95 g, 93%): Bp 102–106 °C (0.48 Torr, bath temp); IR (neat) 2944, 2888, 1257, 1244, 834, 686, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 27H), 0.72–0.78 (m, 2H), 1.43–1.54 (m, 2H), 1.79–1.89 (m, 2H), 3.21 (t, *J*=6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 1.15, 6.49, 6.95, 29.90, 37.36; MS (20 eV) *m/z* (rel intensity) 415 (M^+-Me, 1.2), 359 (M^++2-$SiMe_3$, 26), 358 (M^++1-$SiMe_3$, 19), 357 (M^+-$SiMe_3$, 69), 303 (13), 302 (27), 301 (100). Found: C, 36.11; H, 8.34%. Calcd for $C_{13}H_{35}Si_4I$: C, 36.26; H, 8.19%.

The Reaction of 10 with TTMSS. AIBN (0.10 M benzene solution, 2.0 mL, 0.20 mmol) was added to a benzene (100 mL) solution of **10** (0.861 g, 2.00 mmol) and **2** (0.547 mg, 2.20 mmol) at 80–85 °C. After stirring for 2 h, MeI (0.32 mL, 5.0 mmol) and AIBN (0.20 mmol) were added to the mixture. After stirring for another 2 h, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residual oil was diluted with THF (5 mL) and treated with aqueous NaOH (3M, 2.0 mL) for 10 min. The mixture was poured into saturated aqueous NH_4Cl (30 mL), and extracted with hexane (30 mL x 2). The combined organic layer was dried over Na_2SO_4, followed by concentration and purification by silica-gel column (hexane) to give a mixture (0.504 g, **11**/**12** = 1/2.3) of **11** (27%) and **12** (62%). Analytical pure sample of **11** or **12** was obtained by preparative GLPC.

1,1-Bis(trimethylsilyl)-1-silacyclopentane (11): Bp 68–72 °C (10 Torr, bath temp); IR (neat) 2944, 2890, 2848, 1244, 856, 833, 776, 687, 651, 620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 18H), 0.74–0.81 (m, 4H), 1.51–1.58 (m, 4H); ^{13}C NMR ($CDCl_3$) δ -0.87, 8.02, 29.44; MS (70 eV) *m/z* (rel intensity) 232 (M^++2, 1.7), 231 (M^++1, 3.9), 230 (M^+, 13), 157 (M^+-$SiMe_3$), 142 (11), 129 (18), 117 (19), 103 (10), 73 (100). Found: C, 51.37; H, 11.61%. Calcd for $C_{10}H_{26}Si_3$: C, 52.09; H, 11.37%.

1-[Tris(trimethylsilyl)silyl]butane (12): Bp 74–78 °C (0.70 Torr, bath temp); IR (neat) 2950, 2920, 2890, 1244, 831, 685, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 27H), 0.73–0.79 (m, 2H), 0.88 (t, *J*=7.2 Hz, 3H), 1.26–1.43 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 1.17, 7.17, 13.67, 27.14, 31.45; MS (70 eV) *m/z* (rel intensity) 306 (M^++2, 2.1), 305 (M^++1, 3.8), 304 (M^+, 11), 176 (12), 175 (58), 174 (11), 173 (11), 160 (30), 131 (12), 117 (14), 73 (100). Found: C, 51.04; H, 12.16%. Calcd for $C_{13}H_{36}Si_4$: C, 51.23; H, 11.91%.

Dimethyl 3,3-Bis(trimethylsilyl)-3-silabicyclo[3.3.0]oct-1-ene-7,7-dicarboxylate (14): Bp 95–100 °C (0.28 Torr, bath temp); IR (neat) 2948, 1737, 1435, 1274, 1245, 1198, 1163, 836 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.09 (s, 9H), 0.10 (s, 9H), 0.71 (dd, *J*=13.8, 8.9 Hz, 1H), 1.19 (dd, *J*=13.8, 7.5 Hz, 1H), 1.67 (dd, *J*=12.4, 12.1 Hz, 1H), 2.60 (dd, *J*=12.4, 7.5 Hz, 1H), 2.86 (dm, *J*=17.6 Hz, 1H), 2.94–3.03 (m, 1H), 3.01 (dm, *J*=17.6 Hz, 1H), 3.72 (s, 3H), 3.74 (s, 3H), 5.40–5.43 (m, 1H); ^{13}C NMR ($CDCl_3$) δ -1.05, -0.62, 13.70, 37.27, 42.31, 50.99, 52.72, 61.10, 116.20 (d, *J*=3.4 Hz), 166.55, 172.37, 172.85; MS (20 eV) *m/z* (rel intensity) 386 (M^++2, 2.6), 385 (M^++1, 5.0), 384 (M^+, 17), 369 (39), 311 (75), 225 (94), 167 (35), 135 (37), 105 (30), 89 (100), 73 (63). Found: C, 53.07; H, 8.18%. Calcd for $C_{17}H_{32}O_4Si_3$: C, 53.08; H, 8.38%.

Dimethyl (*E*)-4-Methyl-3-{[tris(trimethylsilyl)silyl]methylene}cyclopentane-1,1-dicarboxylate (15): Bp 110–114 °C (0.40 Torr, bath temp); IR (neat) 2950, 2890, 1739, 1436, 1246, 1202, 1166, 1139, 835, 684, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 27H), 1.08 (d, *J*=6.4 Hz, 3H), 1.66–1.76 (m, 1H), 2.52–2.61 (m,

2H), 2.90 (dt, *J*=17.2, 2.5 Hz, 1H), 3.04 (dm, *J*=17.2 Hz, 1H), 3.72 (s, 3H), 3.73 (s, 3H), 5.30 (q, *J*=2.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.13, 18.55, 40.10, 42.19 (two peaks), 52.69 (two peaks), 58.89, 110.33, 162.06, 172.35 (two peaks); MS (20 eV) *m/z* (rel intensity) 445 (M^++2-Me, 3.3), 444 (M^++1-Me, 6.5), 443 (M^+-Me, 16), 427 (17), 387 (M^++2-$SiMe_3$, 15), 386 (M^++1-$SiMe_3$, 33), 385 (M^+-$SiMe_3$, 100), 281 (36), 206 (10), 205 (45), 163 (11), 147 (18), 117 (20). Found: C, 52.10; H, 8.97%. Calcd for $C_{20}H_{42}O_4Si_4$: C, 52.35; H, 9.23%.

Dimethyl 3-{[tris(trimethylsilyl)silyl]methylene}cyclohexane-1,1-dicarboxylate (16, major isomer): Bp 114–118 °C (0.47 Torr, bath temp); IR (neat) 2948, 2888, 1736, 1435, 1245, 1201, 834, 684, 620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 27H), 1.63–1.74 (m, 2H), 2.04–2.09 (m, 2H), 2.13–2.19 (m, 2H), 2.78 (s, 2H), 3.69 (s, 6H), 5.26 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 1.09, 24.25, 31.19, 34.43, 44.58, 52.51, 57.27, 116.45, 152.62, 171.56; MS (20 eV) *m/z* (rel intensity) 459 (M^++1, 2.2), 458 (M^+, 2.9), 457 (M^+-1, 5.1), 386 (M^++1-$SiMe_3$, 14), 385 (M^+-$SiMe_3$, 45), 333 (11), 332 (27), 331 (100), 263 (10), 205 (35), 163 (12), 147 (16), 121 (12). Found: C, 52.08; H, 9.29%. Calcd for $C_{20}H_{42}O_4Si_4$: C, 52.35; H, 9.23%.

Dimethyl 3-{[tris(trimethylsilyl)silyl]methylene}cyclohexane-1,1-dicarboxylate (16, minor isomer): Bp 117–121 °C (0.35 Torr, bath temp); IR ($CDCl_3$) 2948, 1731, 1246, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 27H), 1.54–1.62 (m, 2H), 2.03–2.08 (m, 2H), 2.23–2.29 (m, 2H), 2.69 (d, *J*=0.9 Hz, 2H), 3.70 (s, 6H), 5.25–5.27 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 1.28, 22.76, 30.93, 38.18, 39.31, 52.41, 55.55, 116.86, 150.91, 171.72; MS (20 eV) *m/z* (rel intensity) 459 (M^++1, 2.6), 458 (M^+, 4.3), 457 (M^+-1, 9.3), 443 (M^+-Me, 10), 386 (27), 385 (73), 332 (26), 331 (100), 205 (60), 163 (26), 147 (31), 131 (25), 117 (25), 73 (56). Found: C, 52.15; H, 9.39%. Calcd for $C_{20}H_{42}O_4Si_4$: C, 52.35; H, 9.23%.

Dimethyl 2-Butyl-3,3-bis(trimethylsilyl)-3-silabicyclo[3.3.0]oct-1-ene-7,7-

dicarboxylate (18): Bp 111–116 °C (0.18 Torr, bath temp); IR (neat) 2950, 2890, 1737, 1435, 1273, 1245, 1199, 1168, 1152, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 18H), 0.68 (dd, *J*=13.6, 9.1 Hz, 1H), 0.85–0.94 (m, 3H), 1.14 (dd, *J*=13.6, 7.1 Hz, 1H), 1.19–1.40 (m, 4H), 1.62 (dd, *J*=12.6, 12.1 Hz, 1H), 2.02–2.18 (m, 2H), 2.55 (dd, *J*=12.6, 7.1 Hz, 1H), 2.84 (s, 2H), 2.86–3.01 (m, 1H), 3.72 (s, 3H), 3.74 (s, 3H); ^{13}C NMR ($CDCl_3$) δ -0.80, -0.21, 13.66, 13.96, 22.93, 31.02, 33.03, 34.38, 42.58, 50.19, 52.71, 52.77, 61.25, 132.43, 157,10, 172.54, 172.90; MS (20 eV) *m/z* (rel intensity) 425 (M^+-Me, 5.4), 368 (M^++1-$SiMe_3$, 15), 367 (M^+-$SiMe_3$, 51), 207 (13), 191 (18), 179 (18), 163 (21), 149 (28), 133 (13), 105 (21), 89 (100). Found: C, 57.05; H, 9.38%. Calcd for $C_{21}H_{40}O_4Si_3$: C, 57.22; H, 9.15%.

Dimethyl 4-Isopropyl-3-{[tris(trimethylsilyl)silyl]methylene}-cyclopentane-1,1-dicarboxylate (20a): Bp 118–122 °C (0.26 Torr, bath temp); IR (neat) 2948, 2888, 1738, 1434, 1244, 1201, 1055, 829, 685, 621 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 27H), 0.62 (d, *J*=6.8 Hz, 3H), 0.93 (d, *J*=6.9 Hz, 3H), 1.48 (d, *J*=14.4 Hz, 1H), 1.91–2.00 (m, 2H), 2.03 (dd, *J*=13.9, 5.9 Hz, 1H), 2.64 (dd, *J*=13.9, 8.9 Hz, 1H), 2.72–2.80 (m, 1H), 3.67 (s, 3H), 3.72 (s, 3H), 5.37–5.39 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 1.04, 8.35, 14.90, 21.11, 27.59, 30.93, 52.11, 52.46, 64.80, 121.19 (d, *J*=3.5 Hz), 151.93, 171.63, 172.81; MS (20 eV) *m/z* (rel intensity) 415 (M^++2-$SiMe_3$, 20), 414 (M^++1-$SiMe_3$, 34), 413 (M^+-$SiMe_3$, 100), 263 (22), 247 (36), 205 (99), 175 (22), 174 (28), 173 (75), 149 (34). Found: C, 53.97; H, 9.68%. Calcd for $C_{22}H_{46}O_4Si_4$: C, 54.27; H, 9.52%.

4-Isopropyl-3-{[tris(trimethylsilyl)silyl]methylene}tetrahydrofuran (20b): Bp 105–109 °C (0.55 Torr, bath temp); IR (neat) 2950, 2890, 1245, 1067, 828, 685, 620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 27H), 0.87 (d, *J*=6.8 Hz, 3H), 0.95 (d, *J*=6.9 Hz, 3H), 1.80–1.93 (m, 1H), 2.51–2.58 (m, 1H), 3.79 (dd, *J*=8.8, 4.8 Hz, 1H), 3.90 (dd, *J*=8.8, 7.0 Hz, 1H), 4.20 (dd, *J*=2.4, 1.3 Hz, 2H), 5.45 (td, *J*=2.4, 1.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.15, 18.12, 20.97, 30.63, 53.19, 70.53, 73.10,

110.24, 159.92; MS (20 eV) *m/z* (rel intensity) 300 (M^++1-$SiMe_3$, 4.3), 299 (M^+-$SiMe_3$, 9.6), 229 (17), 213 (20), 157 (15), 147 (47), 133 (68), 131 (26), 127 (23), 117 (24), 73 (100). Found: C, 54.75; H, 10.94%. Calcd for $C_{17}H_{40}Si_4$: C, 54.76; H, 10.81%.

Dimethyl 3-[Tris(trimethylsilyl)silyl]-2-propenylmalonate (27). Method D: Under argon atmosphere, a benzene (28 mL) solution of dimethyl propargylmalonate **26** (2.38 g, 14.0 mmol), **2** (3.98 g, 16.0 mmol), and AIBN (0.230 g, 1.40 mmol) was heated at reflux for 2 h. The reaction mixture was cooled to room temperature, and concentrated *in vacuo*. The residual oil was purified by silica-gel column (hexane/AcOEt = 10/1) to give the title compound (5.52 g, 94%, *E*/*Z* = 5/4). (*E*)-isomer: Bp 99–103 °C (0.42 Torr, bath temp); IR (neat) 2948, 2890, 1757, 1741, 1437, 1245, 1222, 1151, 836, 686, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 27H), 2.70 (ddd, *J*=7.6, 6.4, 1.3 Hz, 2H), 3.47 (t, *J*=7.7 Hz, 1H), 3.73 (s, 6H), 5.69 (dt, *J*=18.1, 1.3 Hz, 1H), 5.92 (dt, *J*=18.1, 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.70, 36.31, 51.63, 52.51, 125.71, 143.00, 169.30; MS (20 eV) *m/z* (rel intensity) 404 (M^++1-Me, 1.7), 403 (M^+-Me, 4.1), 347 (M^++2-$SiMe_3$, 6.9), 346 (M^++1-$SiMe_3$, 16), 345 (M^+-$SiMe_3$, 49), 307 (14), 306 (27), 305 (100), 205 (18), 189 (13). Found: C, 48.56; H, 9.23%. Calcd for $C_{17}H_{38}O_4Si_4$: C, 48.75; H, 9.14%. (*Z*)-isomer: Bp 115–120 °C (0.55 Torr, bath temp); IR (neat) 2948, 2890, 1757, 1741, 1437, 1339, 1245, 1153, 835, 686, 620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 27H), 2.70 (ddd, *J*=7.9, 6.7, 1.6 Hz, 2H), 3.41 (t, *J*=7.9 Hz, 1H), 3.75 (s, 6H), 5.69 (dt, *J*=13.1, 1.6 Hz, 1H), 6.26 (dt, *J*=13.1, 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.01, 33.96, 51.49, 52.55, 124.88, 142.99, 169.31; MS (20 eV) *m/z* (rel intensity) 404 (M^++1-Me, 1.1), 403 (M^+-Me, 2.7), 347 (M^++2-$SiMe_3$, 12), 346 (M^++1-$SiMe_3$, 28), 345 (M^+-$SiMe_3$, 100), 306 (21), 305 (80), 205 (41), 189 (20), 147 (21), 117 (33), 73 (58). Found: C, 48.76; H, 9.39%. Calcd for $C_{17}H_{38}O_4Si_4$: C, 48.75; H, 9.14%.

Dimethyl Propargyl{3-[tris(trimethylsilyl)silyl]-2-propenyl}malonate (28). A solution of alkenylsilane **27** (5.51 g, 13.2 mmol, *E*/*Z* = 5/4) in THF (15 mL) was added to a suspension of NaH (0.348 g, 15.0 mmol) in THF (20 mL) at room temperature. After stirring for 0.5 h, propargyl bromide (1.72 g, 14.5 mmol) was introduced into the reaction mixture at 0 °C. After 5 min, the mixture was warmed to room temperature and stirred for 4 h. The resulting mixture was poured into water (40 mL), and extracted with AcOEt (50 mL x 2). The combined organic layer was dried over Na_2SO_4, followed by concentration and purification by silica-gel column (hexane/AcOEt = 10/1) to give **28** (5.18 g, 86%, *E*/*Z* = 6/5). (*E*)-isomer: Bp 113–117 °C (0.42 Torr, bath temp); IR (neat) 2948, 2890, 1741, 1437, 1292, 1245, 1204, 836, 685, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 27H), 2.02 (t, *J*=2.7 Hz, 1H), 2.78 (d, *J*=2.7 Hz, 2H), 2.84–2.91 (m, 2H), 3.74 (s, 6H), 5.69–5.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.74, 22.63, 40.05, 52.78, 56.76, 71.39, 78.76, 128.89, 140.54, 170.15; MS (20 eV) *m/z* (rel intensity) 419 (M^++2-C_3H_3, 5.6), 418 (M^++1-C_3H_3, 14), 417 (M^+-C_3H_3, 21), 385 (M^++2-$SiMe_3$, 21), 384 (M^++1-$SiMe_3$, 41), 383 (M^+-$SiMe_3$, 100), 343 (38), 205 (21), 147 (26), 131 (17), 117 (14), 73 (65). Found: C, 52.29; H, 8.53%. Calcd for $C_{20}H_{40}O_4Si_4$: C, 52.58; H, 8.82%. (*Z*)-isomer: Bp 116–120 °C (0.40 Torr, bath temp); IR (neat) 2948, 1740, 1437, 1292, 1246, 1208, 1184, 835, 686, 646, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (s, 27H), 2.00 (t, *J*=2.6 Hz, 1H), 2.86 (dd, *J*=5.9, 2.0 Hz, 2H), 2.88 (d, *J*=2.6 Hz, 2H), 3.74 (s, 6H), 5.74 (dt, *J*=13.5, 2.0 Hz, 1H), 6.20 (dt, *J*=13.5, 5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.14, 23.41, 36.78, 52.79, 56.70, 71.67, 78.83, 126.19, 140.26, 170.31; MS (20 eV) *m/z* (rel intensity) 418 (M^++1-C_3H_3, 4.4), 417 (M^+-C_3H_3, 11), 385 (M^++2-$SiMe_3$, 16), 384 (M^++1-$SiMe_3$, 37), 383 (M^+-$SiMe_3$, 100), 343 (17), 205 (22), 147 (18), 131 (13), 117 (15). Found: C, 52.47; H, 8.55%. Calcd for $C_{20}H_{40}O_4Si_4$: C, 52.58; H, 8.82%.

Dimethyl (*E*)-3-(Tributylstannyl)methylene-4-{[tris(trimethylsilyl)-

silyl]methyl}cyclopentane-1,1-dicarboxylate (29). Cyclization of enyne **28** was performed following Method D by the use of *n*-Bu_3SnH instead of **2**. The reaction of enyne **28** (5.16 g, 11.3 mmol) with *n*-Bu_3SnH (3.96 g, 13.6 mmol) gave the title compound (4.80 g, 57%): Bp 150–165 °C (0.37 Torr, bath temp); IR (neat) 2950, 2922, 2870, 2850, 1739, 1246, 1165, 835, 685, 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 27H), 0.67 (dd, *J*=14.5, 10.5 Hz, 1H), 0.83–1.05 (m, 15H), 1.26–1.65 (m, 13H), 1.73 (dd, *J*=12.3, 11.4 Hz, 1H), 2.39–2.53 (m, 1H), 2.62–2.71 (m, 1H), 2.84 (dm, *J*=16.7 Hz, 1H), 3.02 (dm, *J*=16.7 Hz, 1H), 3.72 (s, 3H), 3.73 (s, 3H), 5.66 (tm, *J*=31.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.25, 9.77, 12.25, 13.72, 27.28, 29.17, 42.30, 42.98, 44.16, 52.69 (two peaks), 57.75, 117.26, 163.21, 172.16, 172.30; Found: C, 51.32; H, 9.28%. Calcd for $C_{32}H_{68}O_4Si_4Sn$: C, 51.39; H, 9.16%.

Dimethyl (*E*)-3-(Bromomethylene)-4-{[tris(trimethylsilyl)silyl]-methyl}cyclopentane-1,1-dicarboxylate (30). Bromine (0.88 M CH_2Cl_2 solution, 1.20 ml, 1.06 mmol) was added dropwise over 5 min to a solution of vinylstannane **29** (0.748 g, 1.00 mmol) in CH_2Cl_2 (10 mL) at -78 °C. After stirring for 25 min, the reaction mixture was warmed to 0 °C and stirred for 5 min. Aqueous $Na_2S_2O_3$ (10 wt%, 0.2 mL) was added to the mixture to destroy an excess of Br_2. After the color of Br_2 disappeared, the mixture was warmed to room temperature. The resulting mixture was treated with saturated aqueous KF (2 mL), and anhydrous KF (1.0 g) for 5 h. White precipitate was removed by filtration through anhydrous Na_2SO_4, and the filtrate was concentrated *in vacuo*. The crude product was purified by silica-gel column (hexane/AcOEt = 10/1) to give vinyl bromide **30** (0.441 g, 82%): Bp 134–138 °C (0.28 Torr, bath temp); IR (neat) 2946, 2888, 1738, 1435, 1297, 1246, 1198, 1167, 836, 688, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 27H), 0.76 (dd, *J*=14.3, 10.8 Hz, 1H), 1.29 (dd, *J*=14.3, 3.3 Hz, 1H), 1.83 (t, *J*=12.2 Hz, 1H), 2.48–2.61 (m, 1H), 2.69 (ddd, *J*=12.4, 6.8, 1.6 Hz, 1H), 2.88 (dt, *J*=18.3, 2.6 Hz, 1H), 3.17 (dm, *J*=18.3 Hz, 1H), 3.73 (s, 3H), 3.75 (s, 3H),

5.94 (q, *J*=2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.20, 11.43, 40.69, 43.05, 43.44, 52.89 (two peaks), 57.26, 99.63 (d, *J*=6.1 Hz), 151.14, 171.61, 171.72. Found: C, 44.08; H, 7.75%. Calcd for $C_{20}H_{41}O_4Si_4Br$: C, 44.67; H, 7.68%.

The Reaction of 30 with TTMSS. According to Method B, a benzene (8.2 mL) solution of vinyl bromide **30** (0.441g, 0.820 mmol) was treated with **2** (0.224 g, 0.900 mmol) in the presence of AIBN (0.10 M benzene sol, 0.82 mL x 5, 0.410 mmol) to give silabicyclo product **14** (0.237 g, 75%).

Dimethyl 3-Methylene-4-{[tris(trimethylsilyl)silyl]methyl}cyclopentane-1,1-dicarboxylate (31). Vinylstannane **29** (0.374 g, 0.500 mmol) was treated with aqueous HCl (1.0 M, 1.0 mL, 1.0 mmol) in acetonitrile (5.0 mL) at room temperature for 3 h. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (30 mL), and extracted with AcOEt (30 mL x 2). The organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residual oil was diluted with CH_2Cl_2 (5 mL) and treated with KF as shown in the synthesis of **30**. The resulting precipitate was filtered, then the filtrate was concentrated *in vacuo*. The crude product was purified by silica-gel column (hexane/AcOEt = 10/1) to provide the title compound: Bp 125–129 °C (0.45 Torr, bath temp); IR (neat) 2946, 2890, 1738, 1435, 1277, 1246, 1212, 1198, 1167, 834, 685, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 27H), 0.71 (dd, *J*=14.5, 10.8 Hz, 1H), 1.33 (dd, *J*=14.5, 3.1 Hz, 1H), 1.74 (dd, *J*=12.3, 11.5 Hz, 1H), 2.40–2.55 (m, 1H), 2.63 (ddd, *J*=12.6, 7.2, 1.2 Hz, 1H), 2.90 (dq, *J*=16.9, 2.2 Hz, 1H), 3.10 (dm, *J*=16.9 Hz, 1H), 3.72 (s, 3H), 3.73 (s, 3H), 4.85 (q, *J*=2.3 Hz, 1H), 4.94 (q, *J*=2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.23, 11.88, 40.31, 41.85, 42.88, 52.74 (two peaks), 57.73, 105.80, 154.38, 172.19 (two peaks); MS (20 eV) *m/z* (rel intensity) 445 (M^++2-Me, 0.8), 444 (M^++1-Me, 1.8), 443 (M^+-Me, 4.7), 387 (M^++2-$SiMe_3$, 16), 386 (M^++1-$SiMe_3$, 31), 385 (M^+-$SiMe_3$, 100), 206 (11), 205 (54), 175 (12), 173 (13), 113 (17). Found: C, 52.08; H, 9.01%. Calcd for $C_{20}H_{42}O_4Si_4$: C, 52.35; H, 9.23%.

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8) A part of this work was published in a communication. K. Miura, K. Oshima, and K. Utimoto, *Chem. Lett.*, **1992**, 2477.

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10) The ratio of *cis*-**4c**/*trans*-**4c** = 3/1 has been reported in ref 7. In contrast, a mixture of *cis*-**4c**/*trans*-**4c** = 1/8 was obtained in our method.

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12) Kulicke *et al.* have not mentioned about the formation of *trans*-silabicyclo compound (*trans*-**3b**) in the reaction of **1b** with **2** in ref 7. Whereas methyl protons of Me_3Si groups of *cis*-**3a** or *cis*-**3b** show two ^1H NMR signals, those of *trans*-**3a** or *trans*-**3b** show one signal because of their C_2 symmetry. In the same way, carbons of Me_3Si groups of *cis*-isomer gave two ^{13}C NMR signals and those of *trans*-isomer gave one signal as shown in experimental.

13) MacroModel was kindly provided by W. C. Still at Columbia University.

14) The reaction of enyne with trialkylstannane gives vinylstannanes exclusively, which form *via* the attack of stannyl radical on terminal acetylenic carbon as shown in ref 2. The addition of stannyl radical to terminal olefinic carbon is reversible, then the radical adduct reverts to original alkene rather than cyclize.

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Publication List

I. Parts of the present thesis have been, or are to be, published in the following journals.

Chapter 2	*Tetrahedron Lett.*, **30**, 4413 (1989).
	Bull. Chem. Soc. Jpn., **63**, 1665 (1990).
Chapter 3	*Tetrahedron Lett.*, **31**, 6391 (1990).
	Bull. Chem. Soc. Jpn., **64,** 1542 (1991).
Chapter 4	*Chem. Lett.*, **1991**, 1319.
	Bull. Chem. Soc. Jpn., **65**, 1513 (1992).
Chapter 5	*Bull. Chem. Soc. Jpn.* in press.
Chapter 6	*Chem. Lett.*, **1992**, 2477.
	Bull. Chem. Soc. Jpn. in press.

II. Other publications not included in this thesis.

(1) Triphenylstannyl Radical or Benzenethiyl Radical Promoted Transformation of 1,1-Dialkoxycarbonyl-2-(1,3-butadienyl)cyclopropanes into 2-Ethenyl-3-cyclopentenes.
K. Miura, K. Fugami, K. Oshima, and K. Utimoto.
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(2) Synthesis of Vinylcyclopentanes from Vinylcyclopropanes and Alkenes Promoted by Benzenethiyl Radical.
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(3) Triethylborane-Induced Hydrodehalogenation of Organic Halides by Tin Hydrides.
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(4) Transformation of N-Tosyl-2-(1,3-butadienyl)aziridine into N-Tosyl-2-ethenyl-3-pyrroline.
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(6) Potassium *t*-Butoxide or Silver Acetate Induced Ring Enlargement of Silacyclobutane into Silacyclopentane. Application to the Synthesis of 1,4-Diol.
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(7) Isomerization of Olefins by Means of R_3SnH-Et_3B and Stereochemical Study on Reduction of Alkenyl Iodides.
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(8) Radical Cyclization of 1-Allyloxy-2-halo-1-silacyclopentane. Application to Stereoselective Synthesis of 1,4,6-Triols.
K. Matsumoto, K. Miura, K. Oshima, and K. Utimoto.
Tetrahedron Lett., **33**, 7031 (1992).

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